RESEARCH PAPER

Enhanced Wettability and Electrolyte Uptake of Coated Commercial Polypropylene Separators with Inorganic Nanopowders for Application in Lithium-ion Battery

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ABSTRACT

In this research, inorganic material type and content influence on coating of commercially available polypropylene (PP) separator were studied for improving its performance and safety as lithium ion battery separator. Heat-resistant nanopowders of Al2O3, SiO2 and ZrO2 were coated using polyvinylidene fluoride (PVDF) binder. Coating effects on the separators morphology, wettability, high temperatures dimensional stability and electrochemical properties were investigated via their scanning electron microscopy images, electrolyte contact angles, electrolyte uptakes, thermal shrinkages analysis and ion conductivities. Furthermore, their performances were studied as the lithium ion batteries separator. All the coated separators have lower thermal shrinkages compared to the commercial neat PP separator. In addition, almost all of the coated separators have shown higher porosities and electrolyte uptakes than those of the commercial neat PP separators. The coated separator with Al2O3 / binder ratio of 8 (MOA8) revealed highest improvement in electrolyte contact angle of 0 °, electrolyte uptake of 218 % (2.04 times increment), ion conductivity of 1.685 mS/cm (1.89 times increment), 52 % porosity compared with the neat PP separator due to proper coating surface morphology, interstitial cavities and a higher Al2O3 dielectric constant than SiO2. In terms of assembled battery discharge capacity reduction after 100 cycles, MOA8 separator showed better cyclic performance as 8.89 % compared with that of the neat PP separator as 16.6 %.

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INTRODUCTION

Owing to advantages such as high energy density, long cycling performance and low self-discharging rate, rechargeable lithium-ion batteries (LIBs) are of the most attractive secondary battery technologies [1] and are used widely in portable electronic equipment [2, 3]. These batteries include main components of anode, cathode, electrolyte and separator [4]. The battery separator, where has key role, is a micro-porous membrane separates anode and cathode electrodes for short circuits prevention and at the same time allows ionic charges to pass through it [4].

Ion transport mechanism through the porous separator membranes is analogous to ion transfer in the electrodes. Ions at the electrode surface

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transfer via specific paths into the electrode pore spaces to reach their active sites where undergo charge transfer there. Therefore, the ion transfer mechanism through the separator membrane has particular importance in the battery performance determining. Important parameters influence the ion motilities through the membranes separators include are: 1) ionic (salvation) structure and the electrolyte's solvent properties, 2) the separator membrane's porous structure, and 3) ions - membrane interactions. Key membrane structural properties such as pore size, porosity, tortuosity, and its chemical composition strongly affect the ions transfer pathways through the linked pores. In practice, it is difficult to individually control these factors during the separator membranes' conventional preparation processes. However, these factors' impact systematic assessment is essential for designing proper separator membranes for lithium ion batteries systems with desirable performances [5].

Various studies have been carried out to produce improved cathode, anode, separator, and other materials for the lithium ion batteries construction with enhanced electrochemical performance and safety and also lower cost [6]. Currently, commercial PP and polyethylene (PE)-based polyolefin separators made by wet or dry processes are used in the lithium ion batteries [7, 8]. Although these separators have good performance and reasonable prices, they have some disadvantages where limited their usage in future required energy storage devices [8]. In particular, their low thermal stabilities and poor wettabilities raise concerns over their assembled batteries safety as well as ion between the electrodes transportation through them [8].

Nanomaterials as a multidisciplinary field encompass physics, chemistry, biology, materials science and engineering. Different applications of nanomaterials in various industrial fields ranging from catalysis and sensing to solar cells, supercapacitors, antibacterial agents and optics are rapidly expanding [9]. Nanomaterials can be prepared via different techniques such as precipitation, sol-gel, sonochemical, microwave, hydrothermal, sol-gel auto-combustion, solid-state reaction, etc. [10-12]. Due to the transport limitations of both electron and ion in lithium ion batteries, nanomaterials are appropriate selections for diminishing the characteristic diffusion length of charge carriers, moreover,

decrease kinetic barriers [13].

Some improvement were achieved on the polyolefin separators for application in the lithium ion batteries due to their improved structural and morphological characteristics and also for performance by coating these separators with inorganic materials/nanomaterials such as zeolites [14, 15], Al_2O_3 [16, 17], TiO_2 [18, 19], ZrO_2 [20] and SiO_2 [21, 22]. Coating the separators with proper inorganic nanomaterials, enable them to absorb higher liquid electrolyte. Increment in the polymer membranes separators' pore size and porosity can significantly improve the ion conductivity, however, at the same time reduce their tensile strength [23]. Additionally, due to the tradeoff between the separators tensile strength and ion conductivity, employing of highly porous separators is also limited [23]. On the other hand, the inorganic nanomaterials-coated separators' electrolyte uptakes and ion conductivities can be improved without reducing their tensile strengths [24, 25]. Coating of the heat-resistant inorganic materials on the polyolefin separators surface also improves their thermal shrinkage and finally assembled batteries safety during their operation [17, 26]. Despite many advantages of nanopowders such as larger specific surface area and higher surface energy [27], research results show that use of smaller inorganic powders lead to their coated separators' lower thermal shrinkages since there are higher nanopowders' number at a given separator surface coating content [24]. It is completely accepted that the parameters like; size, structure and shape have considerable effect on the final properties of the nanopowders [9]. Considering advantages the polyolefin separators coating, various types of inorganic nanopowders have been coated on them [28-30]. In a comparative study, Yu et al. [31] investigated effect of commercial PP separators' top surface Al_2O_3, SiO_2, ZrO_2 particles and ZSM5 zeolite coating using polyvinyl alcohol (PVA) as the binder. They observed that all the coated separators had lower thermal shrinkages than the neat commercial separator. According to their results, differences in the coated separators' thermal shrinkages depend not only on the coated layer material type but also on the inorganic materials and the substrate separator's adhesion degree. Therefore, their higher observed thermal shrinkage of the zeolite coated separator's as 8.9 % (at 130 °C for 30 min) compared with the other coated separators was

attributed to weak adhesiveness of PVA binder for proper adhesion of the zeolite particles on the PP separator surface. They also observed all the separators' liquid electrolyte wettabilities were effectively improved as the neat PP, the Al_2O_3, the SiO_2, the ZrO_2, and the zeolite coated separators' contact angles were measured as 39, 8.4, 0, and 0 °, respectively. Pi et al. [20] coated a commercial PP separator with zirconia particles during a biomineralization process in order to improve the resultant coated separator performance. Their results revealed that the coated separator had excellent dimensional stability even at temperatures around the substrate separator melting point as ∼ 25 % thermal shrinkage at 160 °C. Also, their prepared coated separators had higher wettabilities and electrolyte uptakes resulted in decreased interfacial resistance as well as improved battery performance compared with the commercial PP substrate. In another study [18], a commercially available PP membrane was coated with TiO_2 nanoparticles by Atomic Layer Deposition (ALD) method and it's performance as the lithium ion batteries separator was also investigated. The similar results were also reported in terms of the coated separator improved wettability, thermal shrinkage and lithium ion battery performance. Liu et al. [22] coated SiO_2 particles on both sides of the commercial PP separator using polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) binder and observed that the coated separators' (with SiO_2 to PVDF-HFP ratio of 3) thermal shrinkages decreased (down to about 25 % at 160 °C) while their electrolyte uptakes (up to 2.20 times) and ion conductivities (0.72 mS/cm) enhanced compared with the pristine PP membrane. The coated separators also revealed improved their battery assembled performance in terms of discharge capacity up to 100 cycles and coulombic efficiency (about 99 %). Wang et al. [17] coated Al_2O_3 particles on the commercial PP membrane with phenolphthalein polyetherketone (PEK-C) binder. Their coated separator showed an appropriate electrochemical stability in the assembled lithium ion batteries. In addition, the lithium ion batteries assembled by Al_2O_3 coated separator (with an Al_2O_3 to PEK-C ratio of 4) showed better charge/discharge performance than of the neat PP separator; i. e. discharge capacities of cell batteries assembled by the PP and the Al_2O_3 coated separators after 100 cycles were found as 125.7 and 127.4 mAh/g, respectively. They also reported higher safety for the battery assembled using the PEK-C binder coated separators.

As it can be understood from the carried out literature survey, metal oxide nanopowders are suitable inorganic materials with good chemical, mechanical and thermal properties for coating and in improving the lithium ion batteries separators' structural and performance characteristics. Till now, effects of several types of metal oxides coating on the PP separator using PVDF binder is not reported. In the current study, effects of particles types of Al_2O_3, ZrO_2 and SiO_2 coating using PVDF binder and their contents on the commercial PP separators were simultaneously investigated on the resultant separators' assembled lithium ion batteries' performances. After preparing of different materials coated separators, their morphology, physical properties, and thermal shrinkages were studied using analytical methods.

MATERIALS AND METHODS

Polypropylene separator (Celgard 2400, 41 % porosity) was purchased from Celgard Company. Polyvinylidene fluoride (PVDF, Solvay, Solef®1010) was used as a binder for the separators coating and Polyvinylidene fluoride (Solvay, Solef®5130) was used for the battery cathode preparation. Aluminum Oxide (Al_2O_3, 80 nm), Silicon Dioxide (SiO_2, 0.4 μm) and Zirconium Oxide (ZrO_2, 100 nm) were supplied by US Research Nanomaterials, Inc. Dimethylformamide (DMF, Purity ≥ 99.8 %), Acetone (Purity ≥ 99.5 %) and N-methyl-2-pyrrolidone (NMP, purity of 99 %) were purchased from Merck Co.

Preparation of coated separators

Some slurry mixtures of inorganic materials/ PVDF/ DMF/ acetone were prepared based on the composition showed in Table 1 for coating of the commercial PP separators. The suspensions were prepared by dissolving the prescribed PVDF amount in DMF solvent and then a mixture containing acetone and inorganic materials was added to the former solution (DMF to acetone volume ratio has been set to 1:1). The final mixture's inorganic material and PVDF content was set as 5 Wt. %. In the next step, the obtained mixture was homogenized for 30 min in an ultrasonic bath and then stirred for 3 h. The obtained mixture was casted using a doctor blade on a commercial PP separator and the coated separator was first dried at the room temperature for 30 min. This coating

Table 1. Compositions of the casting solutions for coating the commercial PP separator
(the solvent content of the mixture was 95 wt. %).

Separator Name	PVDF (wt. %)	Inorganic materials type	$\frac{Inorganic\ materials}{PVDF}$ ratio
PP	Commercialized PP separator (Celgard 2400)		
MOA4	1.667	Al_2O_3	4
MOA8	0.556	Al_2O_3	8
MOZ4	1.667	ZrO_2	4
MOZ8	0.556	ZrO_2	8
MOS4	1.667	SiO_2	4
MOS8	0.556	SiO_2	8

process was repeated for several times. The coated separator final thickness was measured using a digital micrometer (Mitutoyo Corp., USA with accuracy of ± 1 μm) and found between 32 and 37 μm. Finally, for complete drying of the coated separators, they were inserted in a vacuum oven at 60 °C for 12 h. Coating was only done on one side of the commercial PP separator. Preparation procedure of the separator coating is schematically illustrated in Fig. 1.

The Prepared Separators Characterization

The separators' surface morphology was investigated using Scanning Electron Microscopy (SEM, Hitachi SU3500, Japan). All the samples were sputtered with gold before observation.

The separators dimensional stabilities data, as commonly reported in terms of their shrinkages percentage, were measured as their dimensions' decrement after holding at 160 °C for 30 min. The separators thermal shrinkages were calculated based on changes in their recorded dimensions at the ambient temperature and 160 °C [32].

A separators porosity (ε) is defined as ratio of its void volume to its apparent geometric volume and calculated by the separator absorbed n-butanol volume using the following equation [33]:
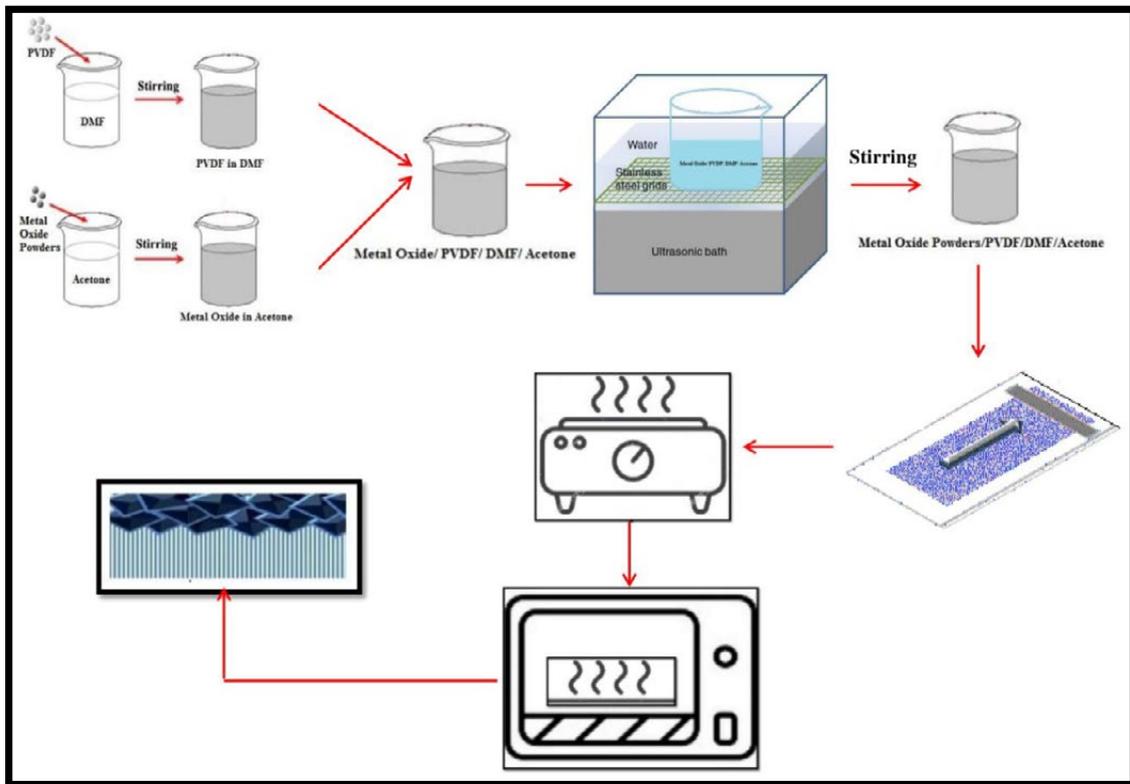

Fig. 1. Schematic representation of the separator's coating procedure.

$$\varepsilon\left(\%\right)=\frac{W_f-W_i}{\rho V}\times100 \qquad (1)$$

where W_f and W_i are the separator n-butanol wetted and dry weights, respectively, ρ is the n-butanol density and V is the separator apparent volume. The dried separator was weighted and then immersed in n-butanol for 1 h and its weight was measured again after the removal of the surface additional n-butanol [34].

A separator contact angle was used to determine its surface wettability by liquid droplets [26] and measured using Dataphysics system (OCA20CA).

A separator electrolyte uptake is expressed as its absorbed electrolyte ratio to the separator's initial weight. Electrolyte uptake was measured using the separator weights before and after liquid electrolyte uptake and calculated using the following equation [33]:

$$\text{Electrolyte Uptake (\%)} = \frac{W_f-W_i}{W_i}\times100 \qquad (2)$$

where W_f and W_i represent the separator weight before and after liquid electrolyte absorption, respectively. The separator was immersed in the liquid electrolyte for 1 h and the sample weight was measured after removal of the excess unabsorbed liquid electrolyte [20].

A separator ion conductivity was examined by sandwiching it between two stainless steels (SS) plates. Using an electrochemical workstation (EIS, Origalys Electrochem) in a frequency range of 0.01 - 100 kHz with amplitude of 10 mV, the impedance data (R_b) can be calculated. Ion conductivity (σ) of a separator was calculated using the following equation [35]:

$$\sigma = d\,/\,A.R_b \qquad (3)$$

where d is the separator thickness and A is the contact surface area between the separator and the SS plates of the battery [35].

The separators electrochemical stability was studied by carrying out linear sweep voltammetry (LSV) experiments applying SS/separator/Li cells with SS working electrodes and a lithium metal counter electrode conducted in the range of 3.0 - 6.0 V with the scanning rate of 3 mV/s.

A LIBs half-cell was assembled by sandwiching the separator between a Li metal as anode and a Li cathode in a glove box. The cathode was prepared by coating the slurry mixture of $LiFePO_4$, carbon black and PVDF (80:10:10 by weight, respectively) in NMP on an aluminum foil and finally it was dried and pressed. 1 M lithium hexafluorophosphate (LiPF6) was used as the electrolyte in a solvent mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) with 1: 1: 1 by volume. The cycling test was carried out at a constant current density of 0.5C/ 0.5C, a voltage limit of 2.5 - 4.2 V and the room temperature using the NEWARE battery testing system [36]. Cycling performance of cells assembled with different prepared separators were examined at 0.5 C for 100 cycles. All the cells were initially cycled twice between 2.5 and 4.2 V at the current rate of 0.1 C for activation [37].
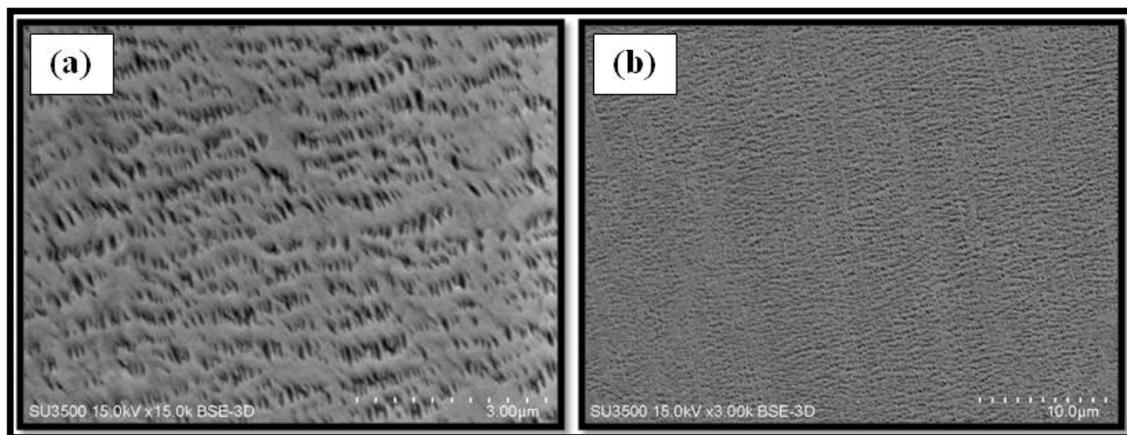

Fig. 2. SEM images of the neat PP separators with different magnification of: (a) 15.0 k, and (b) 3.00 k.
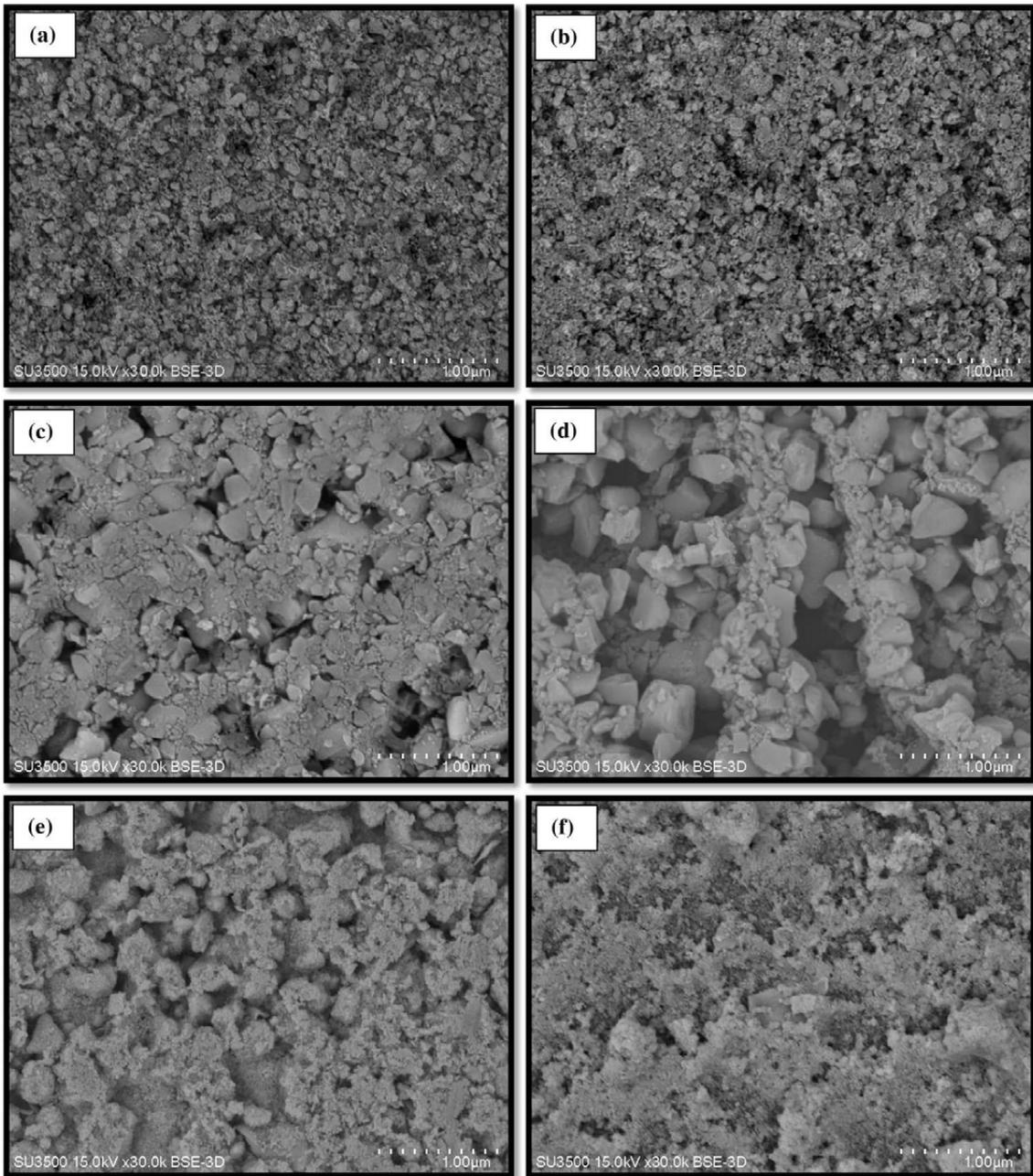
Fig. 3. SEM images of the separators: (a) MOA4, (b) MOA8, (c) MOS4, (d) MOS8, (e) MOZ4, and (d) MOZ8.

RESULTS AND DISCUSSION

Morphology of the Prepared Separators

Fig. 2 and Fig. 3 show SEM images of the separators surface where were quite different in their morphology. Fig. 2. shows the neat PP separator surface image with needle-shaped nanoscale voids formed in its preparation by stretching [34]. Morphology of the coated separators were different from the neat PP separator and also change with the coated layer's inorganic materials/binder ratio variation as well as the coated inorganic materials type (Fig. 2). It should be noted that the separator morphology affects its properties such as thermal shrinkage, electrolyte uptake, porosity, ion conductivity and performance in the battery [22, 24, 38]. As a low thickness coated layer is formed with proper structure and porosity, it's coated

particles interstitial voids will be filled by the liquid electrolyte to provide some interconnected channels lead to easier Li^+ transportation and also results the separator's electrolyte uptake and ion conductivity enhancement. Furthermore, the separators' thermal shrinkage improved due to presence of the heat-resistant inorganic materials on it's surface [22, 24, 38].

As observed, there are close-packed PVDF interconnected Al_2O_3 and SiO_2 particles on the coated separator surface as opposed to the neat PP separator. Separators coated with SiO_2 particles have a uniform structure and there are well-connected network of interstitial voids between these particles. The same structure was also reported in other studies for SiO_2 particles coated on PP separators [22, 24]. Moreover, Al_2O_3 nanoparticles were distributed uniformly on the separator surface and no bare area can be observed there. On the other hand, SEM images of the ZrO_2-coated separator surface show that coating was not well performed and ZrO_2 nanoparticles were clearly agglomerated with PVDF binder, i. e. coated layer of ZrO_2/PVDF was not well formed on the substrate separators. This can be attributed to improper selection of PVDF as a binder for ZrO_2 nanoparticles coating on the PP separator. However, SEM images reveal that SiO_2 and Al_2O_3 particles formed their coated layer on the PP surface using the PVDF binder. The importance of an appropriate binder selection was also reported in other studies [31, 38]. Lee et al. [38] coated the PP separator with Al_2O_3 using PVDF-HFP and PI as the particles binders. They observed that Al_2O_3 particles were agglomerated in the Al_2O_3/PVDF-HFP-coated separator while there was no agglomeration using the PI binder. Yu et al. [31] reported PVA polymer as a proper binder for Al_2O_3, ZrO_2 and SiO_2 particles coating on the PP separator not for the ZSM-5 zeolite particles.

In addition to the inorganic materials type, their content in the coated layer on the separator also affects on the separators morphology. As observed, Al_2O_3 and SiO_2 particles form highly porous coated layer with closed packed structure even though at their higher loadings [25]. On the contrary, agglomeration rate of coated ZrO_2 particles using PVDF binder at higher loadings increased and higher portion of the separator surface was covered by the binder where affected the separator transport performance as discussed in the following paragraphs.

Thermal Shrinkage

In term of the battery safety, its separator must be dimensionally stable [39]. Thermal shrinkages of all the neat and the coated separators were investigated at 160 °C for 30 min [32]. Measured thermal shrinkages of the separators are shown in Fig. 4. As observed, thermal shrinkage of the neat PP separator was relatively high as 43.2 %. The neat PP separator melting point is around 168 °C [24], however, its thermal shrinkage increases at temperatures higher than 110 °C [22]. All coated separators revealed lower thermal shrinkages compared to that of the neat PP separator, where it can be attributed to the coated heat-resistant materials on the separator surface [39].

Considering the thermal shrinkage analysis temperature (well below melting point of inorganic materials studied in the current study), the inorganic material adhesion to the substrate PP separator effect on the coated separators thermal shrinkage is even more profound than that of the inorganic material type itself [31, 38]. Clearly, Al_2O_3, SiO_2 and ZrO_2 have different physical properties and this result in their different bonding strength with the binder [31]. The employed binder in the coated separators creates bonding among particles as well as between them and the substrate PP separator result in uniform coating structure. Hence, the formed bonds among particles as an important factor affects the coated separator structural sustainability. As the adhesion strength among the coated particles as well as between them and the substrate separator get weaker, the coated separator's thermal shrinkage will increases [40].

The ZrO_2-coated separators' thermal shrinkages were higher than the all other coated separators and close to that of the neat PP separator, i. e. MOZ4 and MOZ8 thermal shrinkages were 40.6 and 41.1 %, respectively. This observation also approved that ZrO_2 nanopowders were not properly adhered to the PP separator surface suing the PVDF binder in addition to the obtained results by the SEM images. The same observations were reported by the other researchers [31, 38]. SEM images depicted that MOZ4 and MOZ8 separators' surface were covered by a large amount of PVDF binder. The PVDF melting point is 174 °C as reported by the manufacturer. Although the PVDF melting point is higher than that of the neat PP separator, presence of PVDF on the PP separator surface does not result in a significant
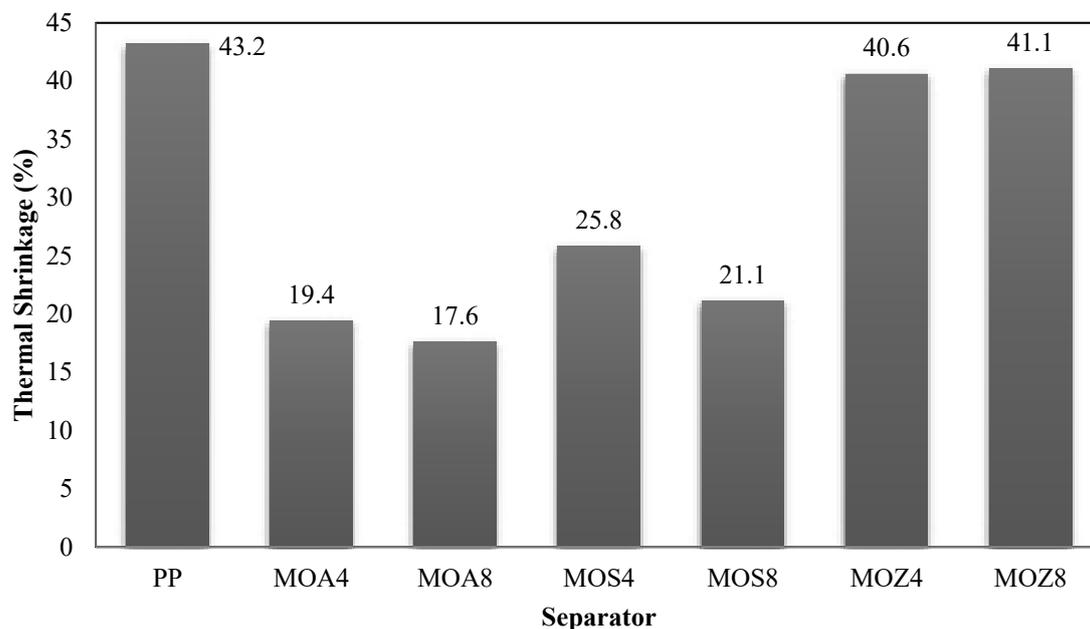
Fig. 4. Thermal shrinkages of the neat and the coated separators at 160 °C for 30 min.

reduction of the PVDF coated separator's thermal shrinkage. This can be due to that the PP separator surface PVDF coating was not sufficiently strong to withstand mechanically against dimensional change during thermal treatment, resulted in higher thermal shrinkages. This reveals that the coated separator thermal shrinkage is affected by synergy between the inorganic material and the polymeric binder [38].

MOS8 and MOA8 separators' thermal shrinkages were found as 21.1 and 17.6 %, respectively. The separators coated by Al_2O_3 and SiO_2 particles improved dimensional stabilities can be attributed to fact that the coating layers can protect the PP separator substrate against thermal shrinkage at high temperatures [31]. This indicates that the Al_2O_3 and the SiO_2 coating layers have strong cohesive strength with the PVDF binder and the PP substrate separator [31]. The Al_2O_3 coated PP separators showed the lowest thermal shrinkage values. This revealed the highest and the lowest cohesive strengths belonged to the Al_2O_3 and the ZrO_2 coated layers, respectively [31, 40]. Moreover, in almost all the coated separators, thermal shrinkages decreased as the inorganic materials content increased, which can be attributed to changes in the coated layer thickness [17] and the higher counts of heat-resistant coated inorganic particles at higher inorganic materials/ binder ratios [41].

Porosity, Wettability and Electrolyte Uptake

In the separators used in lithium ion batteries, Li^+ cations were transferred through voids and channels filled with the liquid electrolyte. Therefore, porosity and electrolyte uptake are important properties of these separators [31, 40]. In the coated separators, size and shape of the coated particles affect on the separators' porosity [31].

Different separators' porosities are shown in Fig. 5. As observed, the neat PP separator porosity was 41 % and those of almost all the coated separators were equal to or greater than that of the neat PP separator. MOS8 separator coated by different SiO_2 particles in size, i. e. simultaneous presence of small and large particles, obtained the highest porosity as 54 %. Obtained high porosity by coating particles with different size was also reported by Yu et al. [31].

Although Al_2O_3-coated separators have a network structure on their surface layer that increases the layer porosity and absorbs higher liquid electrolyte [22, 24], however, they have lower porosities than MOS8 separator due to the smaller size of Al_2O_3 particles (about 80 nm) compared to the other two particles resulted in denser Al_2O_3 surface layer [31]. In addition to the neat PP separator porosity, the coated
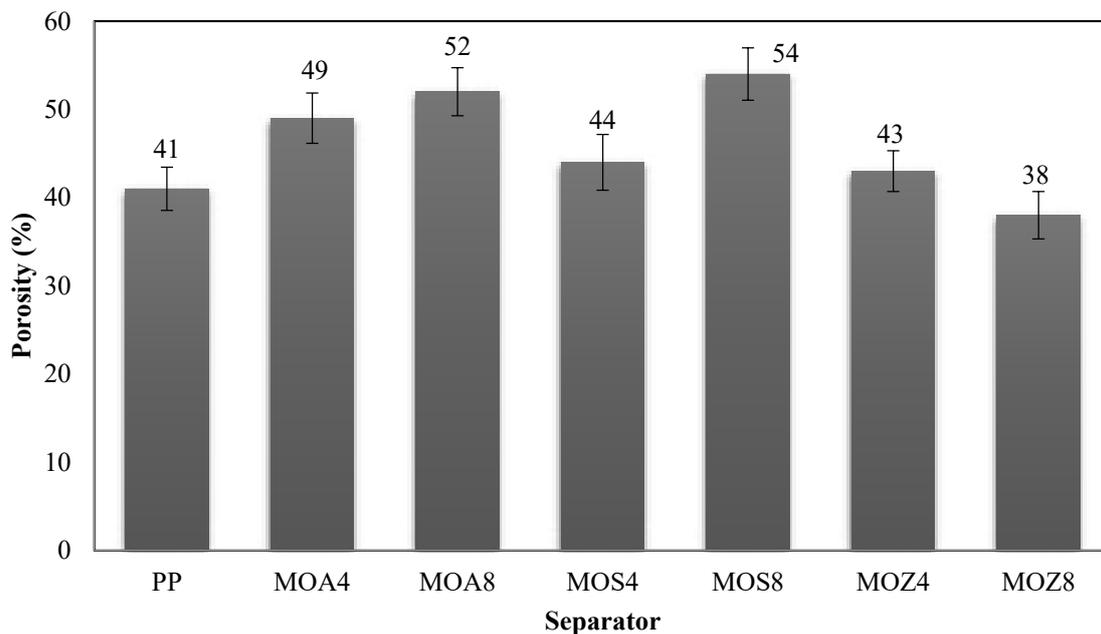
Fig. 5. The neat PP and the coated PP separators measured porosities.

separators total porosity were depended on created voids between the coated particles, i. e. the coated separators' surface morphology [31, 40]. Therefore, due to the surface morphology of ZrO$_2$-coated separators and their aforementioned non-uniform coating, Al$_2$O$_3$-coated separators have higher surface porosity than ZrO$_2$ coated separators. Additionally, this can be attributed to the coated PP separator surface voids (at MOZ4 and MOZ8) filled with the binder body, as was also reported in the other studies [34, 40].

In order to evaluate the prepared separators wettabilities, their electrolyte contact angles were measured [39]. Due to rapid spreading of the electrolyte droplets over the separators' surface, the contact angle measurement within a specific time period of 3 s. Fig. 6 shows effect of the coating layer type on the separators wettability. The contact angle for the neat PP separator was measured as 54.6 ° while contact angles of MOS8, MOA8 and MOZ8 were measured as 4.3, 0 and 42.0 °, respectively. This reveals that the Al$_2$O$_3$ and SiO$_2$ coated separators' wettabilities have significantly improved compared to that of the neat PP separator, i. e. their surfaces are wetted easer with the electrolyte [31]. Besides the coated layer material type, the coated separator wettability surface is also influenced by surface coated layer structural parameters such as its voids size and tortuosity [31]. In the Al$_2$O$_3$ and SiO$_2$ coated

separators, as the inorganic materials/ binder ratio increased, the separator contact angle decreased. This can be attributed to presence higher number of hydrophilic particles at the separator surface [14, 34].

In addition to the separators' contact angle, the electrolyte uptake content is also important due to its effect on being filled with electrolyte at the battery assembling stage as well as the electrolyte maintenance during battery operation [22, 42]. Electrolyte uptakes of the neat PP and the coated separators are shown in Fig. 7. Electrolyte uptakes of the coated separators depend on their wettabilities [14]. Thus, the Al$_2$O$_3$ and the SiO$_2$ coated separators, where exhibited good wettabilities have high electrolyte uptakes, also. This reveals affinity between the coated hydrophilic particles and the electrolyte solvent polar molecules [14, 43]. In addition to the separators wettabilities, which is affected by the coated hydrophilic materials type on the separator surface [31], the electrolyte uptake content also depends on the morphology and porosity of the coated separator layer [16, 22, 42].

In MOA and MOS separators, as the coated particles' number increased and obtained higher porous structures resulted in their increased electrolyte uptakes [25]. Reduced electrolyte uptakes of the ZrO$_2$-coated separators confirmed
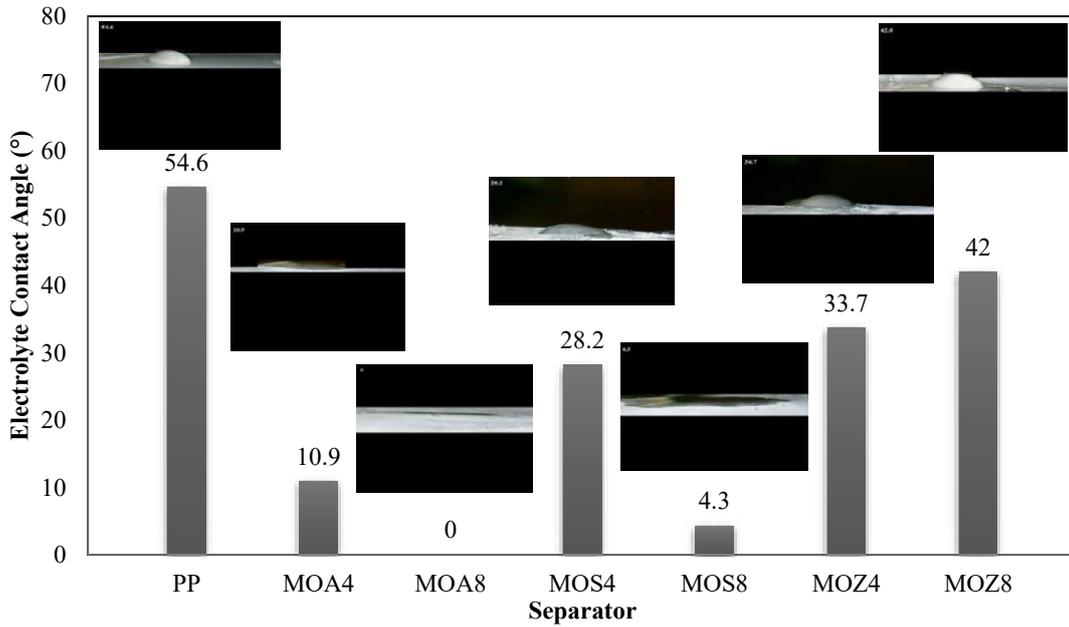
Fig. 6. The neat PP and the coated PP separators' measured electrolyte contact angles.
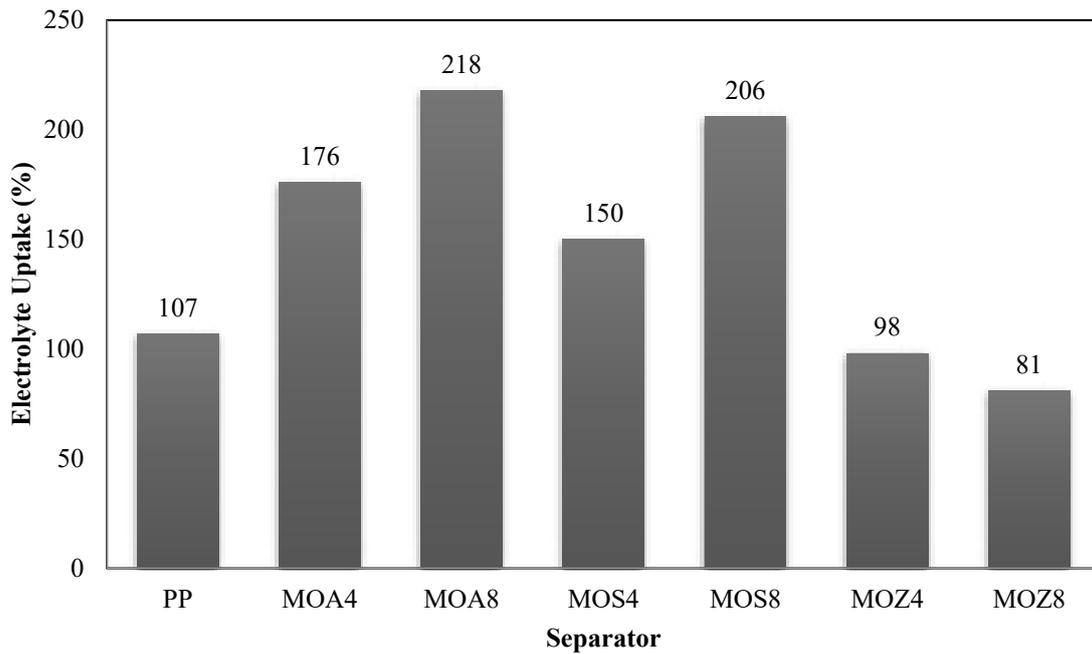

Fig. 7. Electrolyte uptakes of the neat PP and the coated separators.

the predicted reduction in their uptakes due to their specific morphology (as observed in the SEM images) and porosity analysis. The same results has also been reported by Zhang et al. [34].

Ion Conductivity

Ion conductivities of the neat PP and the coated separators impregnated with electrolyte at the room temperature are shown in Fig. 8. The neat PP separator's ion conductivity was measured 0.89 mS/cm and the Al_2O_3 and the SiO_2 coated separators have higher ion conductivities compared to the neat PP separator. On the contrary, the ZrO_2-coated separators were less ion
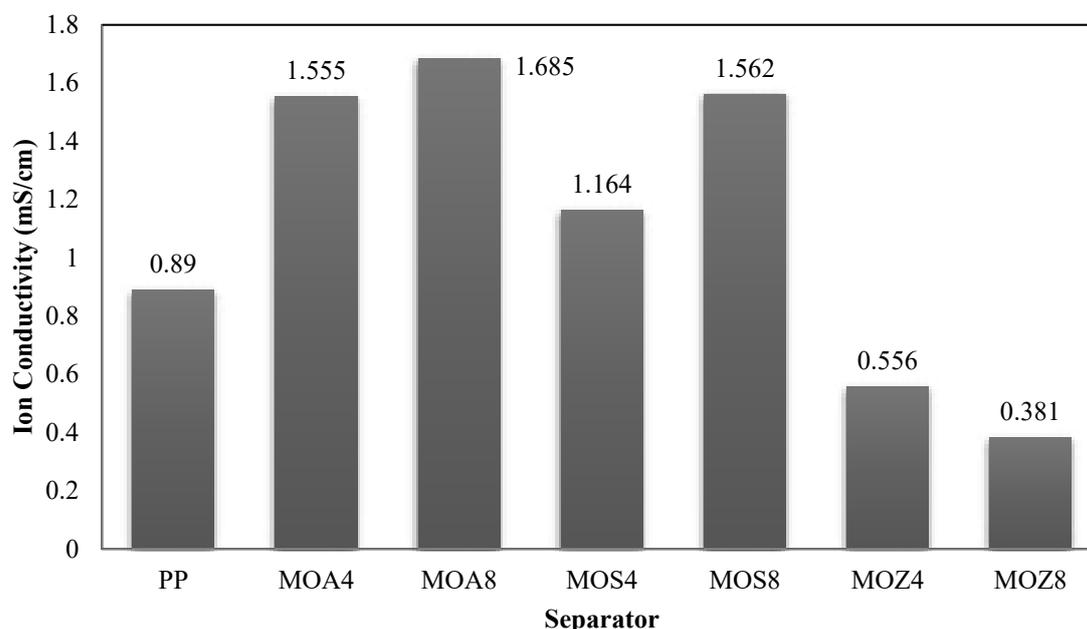
Fig. 8. Ion conductivities of the neat PP and the inorganic coated separators.

conductive compared to the neat PP separator. The observed ion conductivities can be attributed to difference in the separators coated layer structural porosities [31], electrolyte uptakes [22, 42] and dielectric constants [17]. On one hand, lithium ions penetration was facilitated by the separator porosities and electrolyte uptakes increment while decrement in lithium ions resistance transport lead to improvement in ion conductivities [22, 42]. On the other hand, higher dielectric constants of the coated particles resulted in an increment in the lithium ions transportation number as well as increased ion conductivity [16]. Therefore, according to the obtained results of the separators' porosities and electrolyte uptakes, the Al_2O_3 and the SiO_2 coated separators have higher ion conductivities compared with that of the neat PP separator. Dielectric constants of the ZrO_2, the Al_2O_3 and the SiO_2 particles were reported as 25, 9 and 4, respectively [44]. Despite the ZrO_2 particles' higher dielectric constants, the ZrO_2-coated separators revealed no good ion conductivities due to their inappropriate coating and lower porosities and electrolyte uptakes. In contrast, the Al_2O_3 dielectric constant is higher than that of SiO_2 particles, where is another aspect of the Al_2O_3 coated separators' increased ion conductivities compared with those of SiO_2 coated; so MOA8 separator showed the highest ion conductivity as 1.685 mS/cm. The same results were also reported

by Liu et al. [16].

As the inorganic materials / binder ratio increased, the Al_2O_3 and the SiO_2 coated separators' ion conductivities increased; however, those of the ZrO_2 coated separators decreased. These results are consistent with the observed changes in the separators' porosities and electrolyte uptakes [22, 25, 42].

Electrochemical stability

Fig. 9 shows electrochemical stabilities of the pristine PP and MOA8 electrolyte soaked separators. No anodic current was observed below 4.5 V vs Li/Li+ for both separators, revealed that MOA8 has enough electrochemical stability with liquid electrolytes for use in LIBs [34].

For the pristine PP separators, decomposition voltage was found as 4.5 V. The coated separator has higher decomposition potential voltages than the pristine PP separator, which is about 4.7 V. In general, the separators electrochemical stabilities were improved by the Al_2O_3 particle coating and the coated membrane is more stable [17].

Battery Performance

Cyclic performance of cells assembled with the neat PP and MOA8 separators were investigated at a constant current density and the room temperature, as shown in Fig.10. . The assembled cells discharge capacities were reduced by cycling
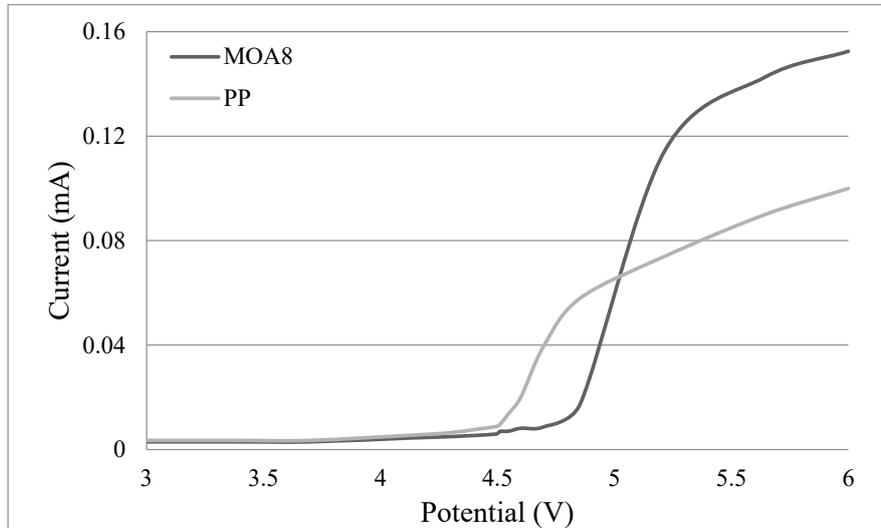
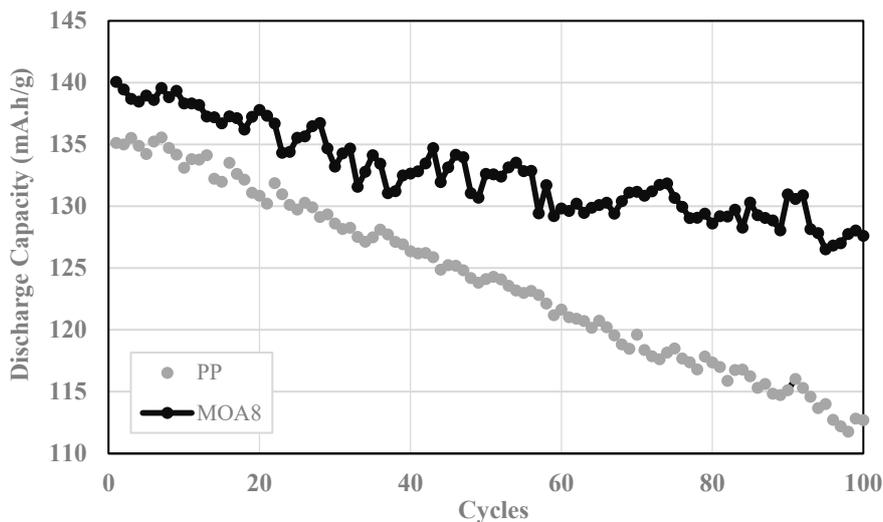Fig. 9. Electrochemical stabilities of the PP and the MOA8 coated separators.

Fig. 10. Cycling performances of the LiFePO4 half cells equipped with the neat PP and the MOA8 coated separators.

due to their increased internal resistances. Higher resistances resulted in lower ion conductivities, ultimately leading to reduced discharge capacities [16]. The cell increased resistance was attributed to the physical changes occurred in their active material and interfaces [22, 24]. This battery discharge capacity declining trend also has been reported in other studies [17, 19, 40].

As observed, compared with the neat PP separator, the coated separators have better discharge capacities. Also, MOA8 separator assembled cell's discharge capacity in the 100th

cycle (127.607 mA.h/g; reduction of 8.89 %) was higher than that of the neat PP separator assembled (112.695 mA.h/g; reduction of 16.6 %). This can be justified by two features as also reported in similar studies [19, 22, 24]. At the First, due to the higher structural porosities and better electrolyte uptakes of the coated separator, their ion conductivities increased and their cells ion transfer were facilitated [16, 24]. The second feature can be attributed to longer electrolyte retention in the coated separators. The electrolyte retention depends on the coating

layer wettability. Higher wettabilities will result in better the retain abilities [19, 40]. Hence, the hydrophilic Al_2O_3 particles coated separators have a higher abilities to retain the liquid electrolyte compared with the neat PP separator with lower hydrophilic characteristic [17, 22]. As a result, the liquid electrolyte leakage will be prevented during the battery cycling results in its cyclability improvement [16, 22, 24].

CONCLUSION

Three different inorganic nanopowders of Al_2O_3, ZrO_2 and SiO_2 were coated on the commercial PP separator using PVDF binder and the coated separators structural properties and their performances as the lithium ion batteries' separator were studied. In addition to effects of various types of inorganic materials, the effects of different ratios of inorganic materials to binder (4 and 8) were also investigated. Investigation of the prepared separators surface morphology revealed no success in the ZrO_2 particles' uniform coating due to their poor bonding to the PVDF binder molecules revealed appropriate binder selection's very high importance for successful coated separators preparation. All the coated separators have lower thermal shrinkages than the neat PP separator; however, their improvements were dependent of the coated inorganic particles type, as there was no significant enhancement in the PVDF coated ZrO_2 particles. Thermal shrinkage of MOZs separators were not considerably reduced despite covering large surface portions of the substrate PP separator with PVDF binder since the separators mainly coated by PVDF and small ZrO_2 contents has no enough mechanical strength to withstand the dimensional changes (i. e. thermal shrinkage) occurred during the separator heat treatment. This revealed the coated separators' dimensional stability was affected by the inorganic materials and the polymeric binder synergy.

Almost all the coated separators possess higher porosities and electrolyte uptakes than those of the neat PP separators and consequently the Al_2O_3 and the SiO_2 coated separators' ion conductivities were found higher than that of the neat PP separator. In addition to the separators' porosity effects, their wettabilities and electrolytic uptakes, the higher Al_2O_3 particles' dielectric constant compared to that of SiO_2 particles dedicated the Al_2O_3 coated separators the highest electrolyte uptakes and ion conductivities. In this

way, MOA8 separator exhibited 2.04 and 1.89 times improvements in their electrolyte uptakes and ion conductivities, respectively, compared with those of the neat PP separator. Due to the improved wettability, electrolyte uptake and ion conductivity of MOA8 separator, considerable improvement in its assembled cell cyclability, i. e. only 8.89 % reduction, was observed compared with the neat PP separator assembled cell as 16.6 % reduction after 100 cycles.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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