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Study on PVDF-HFP/PMMA/CMC Blended Polymer as Membrane for Lithium-Ion Batteries

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The PVDF-HFP/PMMA/CMC blended solid polymer prepared by solvent volatilization method with PVDF-HFP as host polymer matrix and PVDF-HFP/PMMA as blended membrane and then PVDF-HFP/PMMA modified by coating carboxymethyl cellulose(CMC) was introduced in this study to overcome the shortcomings of organic solvent-based liquid electrolyte in lithium-ion batteries. The synthesized copolymers were characterized by FTIR, TGA, XRD, and the results show that PMMA can be well dispersed in PVDF-HFP solution and the addition of CMC can reduce the crystallinity of the polymer membrane, which accelerates the movement of the polymer chain segments and improves the migration rate of lithium-ions. The electrical conductivity of the gel polymer was investigated by AC impedance, and the room temperature ionic conductivity of the gel polymer was up to the order of 10^{-3} S·cm⁻¹, and the electrochemical stability window was 4.8 V. The polymer lithium-ion battery assembled with LiCoO₂ as cathode and lithium sheet as anode has good cycle stability. The lithium metal polymer cell delivered discharge specific capacity with 162.52 mAh.g⁻¹ at the first cycle, and these properties indicate that the modified gel polymer has applicative prospect in polymer lithium-ion batteries.

Keywords: Lithium-ion batteries, Gel polymer, Carboxymethyl cellulose

1. INTRODUCTION

Since the concept of lithium-ion battery was proposed and its commercial application was realized in the early 1990s, lithium-ion batteries (LIBs) as a vital energy accumulator have now become the main power supply for mobile electronic devices, electromobile, power grid energy storage devices, etc [1-3]. However, the capacity deterioration and the security of LIBs have been usually related to the battery ignition or even explosion. The membrane is the insulating layer between the cathode and anode,

and it both acts as an electronic insulator and afford lithium-ions diffusion channels. Usually, a perfect membrane needs to possess favourable electrical insulation, diminutive ionic resistance, high porosity, excellent infiltration, arresting mechanical intensity and electrochemical stability [2,3]. The current commercial lithium-ion battery membrane is mainly polyethylene (PE) or polypropylene (PP) microporous membrane [4,5]. However, catastrophic thermal runaway of LIBs are generally associated with polyolefin microporous membranes and organic liquid electrolytes [6]. Gel polymer electrolytes (GPEs) have got increasing attentions for the integration of characteristics of membranes and electrolytes, which possess good ionic conductivity, good viscoelasticity, arresting thermal stability, broad electrochemical stabilization window, and excellent compatibility with anode and cathode [7-12].

Several types of gel polymer systems with better performance in recent years are polyethylene oxide (PEO) [13,14], polymethyl methacrylate (PMMA) [15,16], polyvinylidene fluoride (PVDF) [17,18], polyacrylonitrile (PAN) [19,20], and polyvinylidene fluoride hexafluoropropylene (PVDF-HFP) [21]. However, all individual gel polymer has intrinsic problems: PAN has poor compatibility with lithium and serious interfacial passivation [22,23]; PVDF has good mechanical strength but is easy to crystallize, which is not conducive to increase ionic conductivity [24]; PMMA can accommodate a large amount of electrolyte but its mechanical properties are poor [25]; and PEO has poor ionic conductivity etc [26]. No single gel polymer electrolyte can meet all the application requirements. Blending is a simple and valid way to improve the conductivity and other properties of polymer electrolytes. Current researches on blending polymer electrolytes have been focused on PVDF, PVDF-HFP, PMMA, and PVC [27-30]. The main reason for the ameliorative effect of polymer electrolytes is the special interactions between polymers (mainly van der Waals forces and hydrogen bonds), which leads to better compatibility of the battery system and significant reduction of the crystalline region of the battery system, thus can enhance the ionic conductivity of the system, and also can reduce the glass transition temperature of the system.

PVDF-HFP is one of the most commonly used materials to prepare gel polymer membrane, which has low crystallinity and thus can form more pores and larger free volume. However, several shortcomings still consist in PVDF-HFP based membrane such as limited ion conductivity for its hydrophobicity, limited thermal stability and undiseriably electrochemical properties which can't meet the stringent requirements for LIBs. Different methods such as amorphization and crystalline polymer blending, surface coating and cross linking have been proposed to solve these shortcomings [31]. PMMA has ester structure, which is similar to organic solvents in liquid electrolytes, accordingly can improve the wetting performance of the co-blended membrane to the electrolyte. What's more, PMMA has good interfacial stability to lithium electrodes and low interfacial impedance to metallic lithium electrodes [32]. Blending PMMA with PVDF-HFP membranes can not only reduce the crystallinity of PVDF-HFP, but also can improve the free volume and porosity of the blended membrane [33]. However, the mechanical strength of PVDF-HFP/PMMA blended membrane is still low and the membrane is prone to fracture.

Carboxymethyl cellulose(CMC) is a natural polymer compound with carboxymethyl groups, which is beneficial to strengthen the bonding the polymer with other substances and is a promising candidate [34]. It provides favourable wettability for its hydrophilic nature and high mechanical intensity. Zhu used a non-solvent method to prepare CMC porous polymer membrane and found that the

room temperature ionic conductivity of CMC porous polymer membrane was 0.48 mS.cm⁻¹ and the lithium-ion migration number at room temperature was 0.46, and in the same time the CMC porous polymer membrane has good electrochemical stability and cycling stability [35].

Host polymers of the GPEs play the vital role of providing mechanical stability and retention capabilities. In this work, we present the results of modification method to coat CMC on PVDF-HFP/PMMA blended membrane to exhibit properties excel each individual component polymer. The PVDF-HFP/PMMA blended membrane was developed and fabricated by the solvent volatilization method, and then the membrane was doped with carboxymethyl cellulose (CMC) by surface coating. The effect of CMC on PVDF-HFP/PMMA membrane performance, mainly including its structure, morphology, thermal stability, ionic conductivity, and cycle performance were examined and confirmed.

2. EXPERIMENTAL SECTION

2.1. Materials.

CMC and PVDF-HFP with an average molecular weight greater than 455,000 and PMMA with an average molecular weight greater than 300,000 were supplied by Aladdin(China), and acetone and N,N-dimethylformamide (DMF) were supplied by Sinopharm(China), 1 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate, dimethyl carbonate, and diethyl carbonate (EC/DMC/DEC = 1/1/1, v/v/v) were obtained from Dongguan Shanshan (China). A commercial PP membrane (Celgard 2400) was used for comparison.

2.2. Preparation of gel polymer.

Firstly, acetone/DMF (3:1 by volume) were mixed as solvent, and then a certain amount of PVDF-HFP and PMMA particles (1:1 by mass) were added and stirred at 60 °C for 4 h until the solution was transparent. Then the mixed solution was coated on one side of the glass plate, and the coating layer was dried at 60 °C for 12 h, then PVDF-HFP/PMMA blended membrane was prepared.

Then 2 g CMC, 50ml water and 2.5 ml DMF were mixed and stirred at 60 °C for 4 h until the solution is transparent. The dried PVDF-HFP/PMMA blended membrane was laid flat on a glass plate and the CMC solution was coated evenly on one side of the PVDF-HFP/PMMA membrane, then the coated membrane was dried under vacuum at 60 °C for 12 h to obtain PVDF-HFP/PMMA/CMC blended membrane.



Figure 1. Schematic drawing for the fabrication of PVDF-HFP/PMMA/CMC blended membrane.

2.3. Characterization

The surface and cross-sectional morphologies of the PVDF-HFP/PMMA/CMC membranes were studied by scanning electron microscope (SEM) (FEI Quanta 450, USA), while the membranes were cooled in liquid nitrogen and broken into two parts mechanically, and then the surface and the cross-sectional SEM micrographs were obtained. The structure of the gel polymers were characterized by Fourier transform infrared spectroscopy (FTIR) (Nicolet JS50, USA) with the wave number range of from 500 to 4000 cm⁻¹. The structure of the gel polymer membranes were analyzed by X-ray diffractometer (XRD) (Bruker D8 Advance, Germany). Thermogravimetric analysis (TGA) were also performed to analyze the shutdown behavior of the membranes with a scan rate of 10 °C/min.

The ionic conductivity of the PVDF-HFP/PMMA and PVDF-HFP/PMMA/CMC membranes soaked with electrolyte at room temperature were measured by sandwiching the membrane between two stainless steel electrodes to assemble a blocking cell. Data were obtained by AC impedance technique with electrochemical workstation (CHI660D, China) over a frequency range from 1 Hz to 100 kHz. The conductivity was then calculated according to equation (1),

$$\sigma = \frac{d}{R*S}$$
 (Equation 1)

where σ denotes the ionic conductivity (S.cm⁻¹); d denotes the thickness of the cell membrane (μ m); R denotes the intrinsic resistance of the membrane (Ω); and S denotes the area of the stainless steel electrode (cm²) [36].

The electrochemical stability window of the gel polymer infiltrated with electrolyte was evaluated by linear sweep voltammetry. It was operated on stainless steel working electrode with lithium sheet as both reference and counter electrode and was operated in the same electrochemical workstation with potential range from 0 to 6 V vs Li/Li⁺ with a scan rate of 5 mV.s⁻¹.

A CR2032 Li/LCO coin cell was assembled by sandwiching the blended polymer between a metallic lithium sheet anode and a LiCoO₂ cathode. The electrochemical performance of the blended polymer electrolyte was tested by Neware battery cycle tester. The test was carried out at C/2 rate with cutoff voltage from 2.75 to 4.2 V. The rate capabilities of the coin cells were assessed by cycling at a incremental discharging current densities from 0.2 to 2 C (0.2, 0.5, 1, 2C, in CC/CV mode for charging and 0.2 C in CC mode for discharging with cutoff voltage from 2.75 to 4.2 V at room temperature.

3. RESULTS AND DISCUSSION

3.1 Structure Analysis

The FTIR was applied to judge the functional groups in samples and to assess changes in the molecules' vibrational patterns in the polymers. In order to explore the composition of blended membrane, FT-IR was tested and analyzed. Figure 2 shows the FT-IR spectra of PVDF-HFP/PMMA and PVDF-HFP/PMMA/CMC blended membranes, from which it can be seen that the peaks in the wave number range from 3000 to 2800 cm⁻¹ are assigned to the vibrational absorption peaks of -CH in -CH₂ and -CH₃, the vibrational absorption peak at 1730 cm⁻¹ is assigned to C=O in PMMA, and the characteristic absorption peaks of PVDF-HFP are the vibrational absorption peak of -CH₂ at 1400 cm⁻¹ and the vibrational absorption peak of C-C at 1072 cm⁻¹, respectively, which indicates the successful preparation of PVDF- HFP/PMMA blended membrane [37]. While the peak at wave number 3420 cm⁻¹ is the asymmetric vibrational absorption peak of -COO in CMC [38]. There is no striking variation in peak positions, which inferrs that there is no obvious structural difference of individual polymers when they are blended. Above analyses indicate that the PVDF-HFP/PMMA/CMC blended membrane has been successfully prepared.



Figure 2. FT-IR spectra of PVDF-HFP/PMMA and PVDF-HFP/PMMA/CMC gel membrane

Figure 3 shows the X-Ray Diffraction Analysis patterns of PVDF-HFP/PMMA and PVDF-HFP/PMMA/CMC blended membrane, it can be seen that there are obvious characteristic diffraction peaks of PVDF-HFP at 2θ =18.4°, 20.1°, 38.9°, and a broad peak of indeterminate phase of PMMA at 2θ =16.9° in the former pattern. With the addition of CMC, new characteristic diffraction peaks were generated at 2θ =28.7°, 46.9°, 47.9°, while the intensity of the broad peak of PMMA was weakened. Meanwhile, the position of each diffraction peak didn't shift, which indicates that the addition of CMC

can reduce the crystallinity of the PVDF-HFP/PMMA polymer membrane and then accelerate the polymer chain segments movement [39]. Above analyses indicate that PMMA can be well dispersed in PVDF-HFP solution and the addition of CMC can reduce the crystallinity of the polymer membrane and accelerate the movement of the polymer chain segments and improve the migration rate of lithium-ions.



Figure 3. XRD patterns of PVDF-HFP/PMMA (a) and (b) PVDF-HFP/PMMA/CMC blended membrane

3.2 Morphology Analysis

Figure 4 shows the surface and cross-sectional morphology of CMC coated modified PVDF-HFP/PMMA gel polymer, which reflect their pore size and distribution. (a) (b) is the surface morphology of the dried membrane, it can be clearly seen that the surface of the PVDF-HFP/PMMA/CMC blended membrane has irregular 3D pore structure, and the size of the pores is ca. 5 μ m, (c) (d) is the cross-sectional morphology of the dried membrane, which presents pore and the membrane become rough, and small voids appear. It can be seen that both the surface and cross section of the membrane have uniform distributed pores. The surface layer has large size pore and the inner layer has small size pore. The uniform distribution of pores and high porosity help to improve the absorption performance and liquid retention performance of the membrane and also can improve ionic transportation.



Figure 4. Surface SEM images of PVDF-HFP/PMMA/CMC at low magnification (a) and high magnification (b), cross section of SEM images of PVDF-HFP/PMMA/CMC at low magnification (c) and high magnification (d), respectively



Figure 5. Thermogravimetric curves of PP, PVDF-HFP/PMMA, PVDF-HFP/PMMA/CMC

3.3 Thermal Stability Analysis

The thermal stability of the commerical PP, PVDF-HFP/PMMA, PVDF-HFP/PMMA/CMC were investigated by thermogravimetric analysis(TGA), as shown in figure 5, the PP membrane is onestep decomposition and starts degrading at ca. 320 °C, and PVDF-HFP/PMMA blended membrane is two-step decomposition and is thermally stable up to 350 °C in the first step and possess a weight loss of ca. 50%, which is due to the poor thermal stability of PMMA [40]. PVDF-HFP/PMMA/CMC is slightly less thermal stably for the poor thermal stability of CMC, which deteriorating the overall thermal stability of the CMC blended membrane, but the weight loss of the blended membrane is less than 5% before 250 °C, indicating that the thermal stability of the polymer can still meet the requirements of LIBs. The PVDF-HFP/PMMA/CMC blended membrane is decomposed in three steps, and there is a small weight loss of 3% at ca. 260 °C, which is likely to be the decomposition of CMC, and the second step of decomposition temperature at 340 °C with a weight loss of ca. 53% should be assingned to the decomposition of PMMA, and the last decomposition step at 430°C, which finally retained 16% of the mass. These results indicate that the addition of CMC slightly reduces the thermal stability of PVDF-HFP/PMMA blended membrane, but the thermal stability of this blended membrane meets the requirements of LIBs, for the PVDF-HFP/PMMA/CMC blended membrane is more stable than commerical PP membrane.

3.4 Electrochemical Stability Window Analysis

The electrochemical stability window is regarded as the working voltage scope of the cell. The difference of oxidation potential gives the stability window of materials from the linear sweep voltammetry profile. The charging cutoff voltage used in LIBs is usually 4.2V, but some high-voltage cathode materials require charging cutoff voltage higher than 4.5V, so we require the working voltage of the polymer electrolyte greater than 4.5V, as shown in Figure 6, when the current rises sharply, it indicates that the membrane begins to oxidize, which means the corresponding voltage is the highest working voltage of the membrane, namely the electrochemical stability window of the membrane [41,42]. The electrochemical stability window of PP, PVDF-HFP/PMMA, PVDF-HFP/PMMA/CMC membrane is 4.5, 4.6, 4.8V, respectively, which means PVDF-HFP/PMMA/CMC membrane has preferable compatibility with carbonate electrolyte and a better electrochemical stability, thus highly compatible for commercial application without any side reaction in LIBs. The experimental results indicate that the PVDF-HFP/PMMA/CMC membrane has the highest electrochemical stability. We conclude that the addition of CMC can optimize the electrochemical stability of the polymer membrane. What's more, The electrochemical stability window of the cells assembled by PVDF-HFP/PMMA/CMC exceed cells assembled by commerical PP membrane and Li's PVDF-IGMO membrane, but a little lower than cells assembled by Zhong's PMMA-MAH membrane and Wu's PP-PMMA membrane[14,18,28].



Figure 6. PP, PVDF-HFP/PMMA, PVDF-HFP/PMMA/CMC Linear scanning voltammetric curves

3.5 Ionic Conductivity

The ionic conductivity is an important indicator of polymer electrolytes, which characterizes the transport rate of lithium-ions in the membrane. Research on electrical conductivity spectra can offer the perspective of charge transport mechanism and ion dynamics of gel polymer electrolytes. The hydrophobic nature and the dense structure of pure PVDF-HFP result in a low ion conductivity and restrict its extensive applications in LIBs. In order to optimize the membrane ion conductivity, PDVF-HFP/PMMA is coated by cellulose to enhance the wettability and build the microporous structure. Figure 7 shows the AC impedance spectra of PP, PVDF-HFP/PMMA, and PVDF-HFP/PMMA/CMC, and low-frequency straight line is followed by high-frequency semicircle. A high-frequency semicircle represents the shunt combination of a resistor and a capacitor whereas the straight line at low- frequency region means the charge accumulation, and the intersection of the curves with the real axis in the figure is approximated by the intrinsic resistance R of the membrane [43], from which we can derive the intrinsic impedance values of 15.6, 4.5, and 3.4 ohm for PP, PVDF-HFP/PMMA, and PVDF-HFP/PMMA/CMC, respectively. The ionic conductivity of PP, PVDF-HFP/PMMA, and PVDF-HFP/PMMA/CMC can be calculated by equation (1) as 0.95, 3.279, and 4.388 mS.cm⁻¹, respectively. The results show that the addition of CMC can optimize the ionic conductivity of the blended membrane, which is due to the fact that the addition of CMC improves the absorption and retention rates of the electrolytes, which means the higher corresponding amount of free Li⁺ and the lower the intrinsic resistance of the membrane, and therefore the larger corresponding ionic conductivity [44]. The ionic conductivity of the cells assembled by PVDF-HFP/PMMA/CMC outclass cells assembled by commerical PP membrane and Zhong's PMMA-MAH membrane and Li's PVDF-IGMO membrane and Cao's PVDF-HFP/PMMA/TiO₂ membrane[14,18,45].



Figure 7. AC impedance spectra of PP, PVDF-HFP/PMMA, PVDF-HFP/PMMA/CMC

Membrane	Electrolyte	Ionic	Operating	Discharge capacity	Capacity	Literature
		conductivity	window/V	Mah/g (R.T.)	retention/%	
		mS/cm				
PVDF-IGMO	LiClO ₄	3.82	2.5-4.25	168.4(0.1C,1st cycle)		[18]
	EC/PC/DMC			151.6(0.1C,50th cycle)	90	
PVDF-	LiPF ₆ EC/DEC	3.4	2.75-4.4	168.0(0.5C,1st cycle)		[45]
HFP/PMMA/				160.4(0.5C,50th cycle)	95	
TiO ₂						
PVDF-HFP/SiO ₂	LiPF6 EC/DEC	1	3.0-4.2	153.0(0.5C,1st cycle)		[46]
				150.0(0.5C,100th cycle)	94	
PVDF-HFP	LiNfO	1	3.0-4.15	164.0(0.1C,1st cycle)		[47]
	EMImNfO			161.0(0.1C,45th cycle)	98.1	
PVDF-	LiPF ₆	4.43	2.75-4.2	162.5(0.2C,1st cycle)		This work
HFP/PMMA/CMC	EC/DMC/DEC			152.0(0.2C,50th cycle)	93.5	
				140.0(0.2C,100th cycle)	86.2	

Table 1. Performance comparison of the Li/LCO cells assembled with different polymer as membrane

3.6 Cell Cycle Performance

The galvanostatic charge/discharge cycle test is a credible method to assess the electrochemical capacitance of materials. In order to comprehensively assess the electrochemical properties of the prepared polymer membranes, PP, PVDF-HFP/PMMA, PVDF-HFP/PMMA/CMC membranes were assembled into LiCoO₂/GPE/Li half-cells for cycle performance tests, and Figure 8 shows the initial charge/discharge curves of these half-cells, and the initial discharge specific capacity of PP, PVDF-HFP/PMMA, and PVDF-HFP/PMMA/CMC was 150.79, 155.092, and 162.520 mAh.g⁻¹ respectively. indicating that CMC can improve the charge/discharge capacity of the membrane, which is attributed to the CMC coated PVDF-HFP/PMMA membrane enhances the ionic conductivity, and thus enhances the compatibility of the membrane with the electrolyte. Above analyses show that PVDF-HFP/PMMA/CMC blended membrane electrolyte has applicative prospect. Figure 9 shows the graph of 100 cycles of PP, PVDF-HFP/PMMA and PVDF-HFP/PMMA/CMC membranes assembled into half-cells at 0.2 C current density. The capacity retention rates of PP, PVDF-HFP/PMMA and PVDF-HFP/PMMA/CMC membranes after 100 cycles was 76.4%, 79.74% and 86.22%, respectively. The above analysis results showed that the PVDF-HFP/PMMA/CMC blended membrane not only has high charge/discharge capacity but also has good cycling stability, which may be attributed to the good liquid electrolyte retention and electrochemical interface stability possessed by the blended membrane. In contrast with previous study as depicted in table 1, the room temperature cycle performance of cells assembled by PVDF-HFP/PMMA/CMC is better than cells assembled by PVDF-IGMO, and is comparable to the cells assembled by other gel membranes [18,45-47].



Figure 8. Charge/discharge curve of LiCoO₂/GPE/Li with PP, PVDF-HFP/PMMA, PVDF-HFP/PMMA/CMC



Figure 9. Cycle performance of LiCoO₂/GPE/Li with PP, PVDF-HFP/PMMA, PVDF-HFP/PMMA/CMC at 0.2C

3.7 Cell Rate Performance

To assess the rate capability of the membranes, the assembled cells were charged/discharged at incremental rates at room temperature.



Figure 10. Cycle performance of LiCoO₂/GPE/Li with PP, PVDF-HFP/PMMA, PVDF-HFP/PMMA/CMC at different rates

As the discharge rate increases, the difference of membrane performance becomes more pronounced as shown in Figure 10, from which we can see that the PVDF-HFP/PMMA/CMC shows relatively higher discharge specific capacity and better cycling stability under all rate conditions. The

discharge specific capacity of the PVDF-HFP/PMMA/CMC reaches 139.733 mAh.g⁻¹ at 2 C current density, which is higher than that of the PVDF-HFP/ PMMA (131.719 mAh.g⁻¹) and PP (100.803 mAh.g⁻¹). The higher discharge capacity of the blended membrane electrolyte with the addition of CMC is due to its higher absorption rate and higher ionic conductivity. These results indicate that the charge and discharge capacity of the cells with all gel polymer electrolytes are obviously decreased along with the C-rate increases, which is assigned to the polarization effect [48].

4. CONCLUSIONS

In summary, a porous gel polymer based on PVDF-HFP/PMMA/CMC from the perspective of polymer blending compatibility was successfully prepared in this study. PVDF-HFP/PMMA blended polymer membrane was first fabricated via solvent volatilization method, and then this membrane was doped with carboxymethyl cellulose (CMC) by surface coating to prepare PVDF-HFP/PMMA/CMC blended polymer membrane, and the synthesized copolymers were characterized by FTIR, TGA , XRD, the results show that PMMA can be well dispersed in PVDF-HFP solution and the addition of CMC can reduce the crystallinity of the polymer membrane and accelerate the movement of the polymer chain segments and improve the migration rate of lithium-ions. The copolymer also has good thermal stability, excellent electrochemical stability, and room temperature ionic conductivity can reach 4.388 mS.cm⁻¹, which is much more higher than Li/LCO coin cells assembled by other gel membranes. What's more, the membrane has uniform distributed pores on the surface and cross-section, which can improve the liquid absorption and retention rate of the membrane, indicating that this blended membrane has applicative prospect.

NOTES

The authors declare no competing financial interest.

References

- 1. M. Deka and A. Kumar, J. Power Sources, 3(2011)1358.
- 2. J. N. Zhang, L. Zhang, F.C. Sun and Z.P. Wang. *Ieee Access*, 6(2018)23848.
- 3. Q.Q. Liao, M.M. Mu, S. Q. Zhao, L. Z. Zhang, T. Jiang, J. L. Ye, X. W. Shen and G. D. Zhou, *Int. J. Hydrogen Energy*, 42(2017)18817.
- 4. M. F. Lagadec, R. Zahn and V. Wood, J. Electrochem. Soc., 165(2018) A1829.
- 5. Y. Saito, S. Takeda, J. Nakadate, S. Tomoya and T. Cho, J. Phys. Chem., 123(2019)21888.
- 6. A.A. Heidari and H. Mahdavi, Chem. Rec., 20(2020)570.
- 7. M. H. Ryou, M. L. Yong, K. Y. Cho, G. B. Ham, J. N. Lee, D. J. Lee, J.W.Cho and J.K.Park, *Electrochim. Acta.*, 60(2012) 23.
- 8. M. K. Zhao, X. X. Zuo, C. Y. Wang, X. Xiao, J.S. Liu and J.M. Nan, *Ionics*, 22(2016)1.
- 9. S. Tang, W. Guo and Y. Z. Fu, Adv. Energy Mater, 11(2020)2000802.
- 10. X. F. Song, Y. N. Zhang, Y. W. Ye, Z. F. Liu, F. Cheng and H. R. Li, ACS Appl. Energy Mater.,

3(2020)4906.

- 11. X. Shen, H. M. Hua, R. Y. Li, T. X. Hu, D. Z. Wu, P. Zhang and J. B. Zhao, *Polymer*, 201(2020)122568.
- 12. J. R. Gou, W. Y. Liu and A. M. Tang, J. Mater. Sci., 55(2020)10699.
- D. F. Miranda, C. Versek, M. T. Tuominen, T. P. Russell and J. J. Watkins, *Macromolecules*, 46(2013)9313.
- 14. X. P. Zhong, Y. Huang, H. J. Cao, Y. H. Lin, B. Liu, A. M. Song, Z. M. Chen, S. H. Tang, M. S. Wang and X. Li, *J. Solid State Electrochem.*, 21(2017)849.
- 15. C. C Sun, A. H. You and L. L. Teo, Polym Plast. Technol. Eng., 39(2019)612.
- 16. A. Hosseinioun, P. Nürnberg, M. Schönhoff, D. Diddens and E. Paillard, RSC Adv., 9(2019)27574.
- 17. C.Y. Cao, L. Tan, W. W. Liu, J. Q. Ma and L. Li, J. Power Sources, 248(2014)224.
- 18. W. L. Li, Z. B. Zhu, W. J. Shen, J. J. Tang, G. Yang and Z. X. Xu, RSC Adv., 6(2016) 97338.
- 19. N. Sabetzadeh, A. A. Gharehaghaji and M. Javanbakht, Solid State Ion, 325(2018) 251.
- 20. W. G. Chong, K. B. M. Isa, L. Othman, N. H. Zaiol, S. M. Samin and Z. Osman, *Adv. Mat. Res.*, 1024(2014)335.
- 21. S. H. Song S, J. W. Wang, J. W. Tang, R. Muchakayala and R. Ma, Ionics, 23(2017) 3365.
- 22. X. Tang, R. Muchakayala, S. H. Song, Z. Y. Zhang and A. J. Polu, J. Ind. Eng. Chem., 37(2016)67.
- 23. N. K. Jyothi, K. K. V. Ratnam, P. N. Murthy and K. V. Kumar, Mater Today Proc., 3(2016)21.
- 24. F. L. Zhou, H. Y. Liao and Z. Z. Zhang, Ionics, 26(2020)3893.
- 25. H. Y. Liu, L. L. Liu, C. L. Yang, Z. H. Li, Q. Z. Xiao, G. T. Lei and H. Y. Ding, *Electrochim. Acta*, 121(2014)328.
- 26. X. Shen, R. Y. Li, H. S. Ma, L. Q. Peng, B. Y. Huang, P. Zhang and J. B. Zhao, *Solid State Ion*, 354(2020)115412.
- 27. N. H. Idris, M. M. Rahman, J. Z. Wang and H.K. Liu, J. Power Sources, 201(2012)294.
- 28. D. Z. Wu, J. L. He, M. Z. Zhang, P. H. Ni, X. F. Li and J. K. Hu, J. Power Sources, 290(2015)53.
- 29. Y. Huang, B. Liu, H. J. Cao, Y. H. Lin, S. H. Tang, M. S. Wang and X. Li, J. Solid State Electrochem., 21(2017)2291.
- 30. Z. Zheng, Q. Cao, X. Y. Wang, N.Ma and Y. Wang, *Ionics*, 18(2012)47.
- 31. D.Y. Song, C. Xu, Y. F. Chen, J. R. He, P. J. Li, W. Lin and F. Fu, Solid State Ion, 282(2015)31.
- 32. A. Hosseinioun and E. Paillard, J. Memb. Sci., 594(2020)117456.
- 33. K. Mishra, T. Arif T, R. Kumar and D. Kumar, J. Solid State Electrochem., 23(2019) 2401.
- 34. Y. M. Deng, X. N. Song, Z. Ma, Z. H. Zhang, D. Shu and J. M. Nan, *Electrochim. Acta*, 212(2016)416.
- 35. Y. S. Zhu, S. Y. Xiao, M. X Li, Z. Chang. F. X. Wang, J. Gao and Y. P. Wu, *J. Power Sources*, 288(2015)368.
- 36. K. Gohel and D. K. Kanchan, J. Adv. Dielectr, 8(2018)1850005.
- 37. L. N. Sim, S. R. Majid and A. K. Arof, Vib. Spectrosc., 58(2012)57.
- 38. C. Subbu, S. Rajendran, K. Kesavan and R. Premila, Ionics, 22(2016)229.
- 39. P. S. Kumar, A. Sakunthala, M. V. Reddy and P. Moni, Solid State Ion, 319(2018) 256.
- 40. K. Gohe and D. K. Kanchan, J. Mater. Sci., 30(2019)12260.
- 41. W. Y. Chen, Y. B. Liu, Y. Ma and W. X. Yang, J. Power Sources, 273(2015)1127.
- 42. S. Jamalpour, M. Ghahramani, S. R. Ghaffarian and M. Javanbakht, Polymer, 195(2020) 122427.
- 43. W. Zhai, H. J. Zhu, L. Wang, X. M. Liu and H. Yang, Electrochim. Acta, 133(2014) 623.
- 44. A. K. Arof, S. Amirudin, S. Z. Yusof and I.M. Noor, Phys. Chem. Chem. Phys, 16(2014)1856.
- 45. J. Cao, L. Wang, M. Fang, X. M. He, J. J. Li, J. Gao, L. F. Deng, J. L. Wang and H. Chen, *J. Power Sources*, 246(2014)499.
- 46. Y.S. Lee, S. H. Ju, J. H. Kim, S. S. Hwang, J. M. Choi, Y. K. Sun, H. Kim, B. Scrosati and D. W. Kim, *Electrochem. Commun.*, 17(2012)18.
- 47. K. Karuppasamy, P. A. Reddy, G. Srinivas, R. Sharma, A. Tewari, G. H. Kumar and D. Gupta, *J. Solid State Electrochem.*, 21(2017)1145.

48. B. Liu, Y. Huang, L. Zhao L, Y. X. Huang, Y. H. Lin, M. S. Wang, X. Li and H. J. Cao, *J. Memb. Sci.*, 564(2018) 62.

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