Electrochemical Properties of Gel Polymer Electrolytes Prepared by Poly(vinyl acetate) Copolymers

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We have studied the electrochemical properties of gel polymer electrolytes prepared by poly(vinyl acetate) copolymers. All of the gel polymer electrolytes showed elasticity, free standing property and ionic conductivities over 0.5 mS/cm in certain compositions. The vinyl acetate moiety could increase the affinity of copolymer toward carbonate-based liquid electrolytes, but silica was needed to prepare elastic and stable gel polymer electrolyte. The effect of silica on the different types of the copolymer matrix is discussed in detail. The gel polymer electrolyte prepared by using poly(methyl methacrylate-co-vinyl acetate)(PMVC) especially showed stable ionic conductivity over 1×10^{-3} S/cm with a reasonable mechanical strength and electrochemical stability window above 4.8 V among the gel polymer electrolytes that tested in this study.

Keywords : Gel polymer electrolyte, Ionic conductivity, Lithium polymer battery, Poly(vinyl acetate).

Introduction

The most suitable battery type is one that contains a large amount of energy in a small package, light weight and safety. This is found in the lithium polymer battery (LPB) which uses a polymer electrolyte. The performance of the polymer electrolyte is a key factor in making a high performance LPB. The performance required of polymer electrolyte for LPB can be summarized as follows: 1) high ionic conductivity over 0.5 mS/cm, 2) chemical and electrochemical stability, 3) mechanical strength and flexibility, 4) thermal stability, 5) environmental safety, and 6) high affinity with liquid electrolyte. Several researchers have studied gel polymer electrolyte as one of the most suitable polymer electrolytes. The reported polymer materials for gel polymer electrolytes are as follows; polyacrylonitrile (PAN),[1-3] poly(vinyl chloride) (PVC),[4,5] poly(vinylidene fluoride) (PVDF) and its derivatives.[6-9] These gel polymer electrolytes have enough mechanical strength, but there still remains the exudation problem of liquid electrolyte due to the phase separation between a polymer matrix and an encapsulated liquid electrolyte.

Modified copolymers with two or more functional monomers have been suggested as a solution to the leakage problem of liquid electrolyte and to improve mechanical strength. M. Yamazaki *et al.* prepared several gel polymer electrolytes by using vinylic copolymers such as vinyl chloride-acrylonitrile, methyl acrylate-vinyl chloride copolymer, styrene-acrylonitrile copolymer etc. to enhance ionic conductivity and charge-discharge cycle performance.[10] T. Ichino *et al.* prepared stable gel polymer electrolytes with styrene-butadiene copolymer latex and acrylonitrile-butadiene copolymer latex to ensure high ionic conductivity and mechanical strength.[11]

Introduction of a functional moiety that has strong polarity, such as vinyl acetate, can improve the affinity of polymer matrix toward carbonate-based liquid electrolyte and alleviate the solvent exudation problem of its gel polymer electrolyte. H. Sung *et al.* reported on a gel polymer electrolyte using modified PVC with vinyl acetate as a solution to the problem of solvent exudation.[12] They, however, adopted a cosolvent, such as *N*-methyl pyrrolidinone (NMP) or *N,N*-dimethyl formamide (DMF), to prepare stable gel polymer electrolyte due to the lack of solubility of the PVC segment toward carbonate-based liquid electrolytes, even though 10 mol% of vinyl acetate was incorporated. Although poly(vinyl chloride-co-vinyl acetate) gel polymer electrolyte shows ionic conductivity exceeding 1 mS/cm and an electrochemical stability window up to 4.9 V, NMP or DMF is rarely used as a cosolvent for liquid electrolyte in lithium secondary batteries due to the deterioration of charge/discharge performance.

In the present study, we also study the electrochemical properties of gel polymer electrolytes by using vinyl acetate incorporated copolymers that are rarely reported in the electrochemical study of a polymer matrix for a gel polymer electrolyte. Fumed silica was added to prepare stable gel polymer electrolytes without using other additive solvents, and the effect of fumed silica on the ionic conductivity of the

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gel polymer electrolytes is examined in detail.

Experimental Section

Materials and reagents. We used poly(vinyl acetate) (PVAc) copolymers described in Table 1 and 2. PMVCs were synthesized by using emulsifier-free emulsion polymerization[13] and others were purchased from Aldrich Company. Fumed silica, of which the surface OH group was silanized, was purchased from Cabot Co. and used as an inorganic filler. A solution of 1 M $LiClO_4$ in ethylene carbonate (EC)/propylene carbonate (PC) mixture (1 : 1 by vol%) was used as a liquid electrolyte and purchased form Mitsubishi Chemical.

Preparation of gel polymer electrolyte. PVAc copolymers were completely dissolved in tetrahydrofuran (THF) to give a homogeneous solution. Fumed silica and liquid electrolyte were added into the copolymer solution, which was vigorously stirred to prepare a casting solution for 2 hrs. The gel polymer electrolytes were fabricated by casting the copolymer solution onto a release paper with a gap of 0.5 mm. The cast films were allowed to dry at 25 ºC in an argon-filled dry box for 1 hr. The thickness of the resulting gel polymer electrolyte films was around 80 μm.

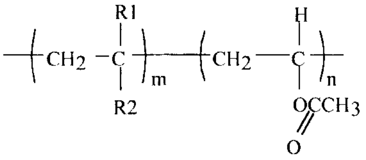
Electrochemical analysis. The ionic conductivity was measured with IM6 Impedance Spectrum Analyzer (Zahner Co.) with a frequency range of 10 Hz to 1 MHz and an amplitude of 10 mV. The measurement cell was prepared by sandwiching the gel polymer electrolyte film between two stainless steel electrodes in a dry box. The effective area for measurement was 4 cm^2. A linear sweep voltammetry was carried out with the cell consisting of the stainless steel electrode as a working electrode and lithium metal as a counter and reference electrode.

Battery test was carried out with TOYO battery cycler. The test cell was assembled by sandwiching gel polymer electrolyte between a composite carbon anode and a composite cathode. The composition of the composite electrodes is listed in Table 3. MCMB2528 (OSAKA Gas Co.) and $LiMn_2O_4$ (FMC Co.) were used as active materials for anode and cathode, respectively.

Results and Discussion

Ionic conductivity. We used two different types of PVAc copolymers that have acrylic and ethylenic moieties in the

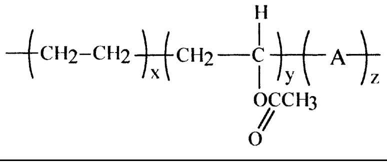
Table 1. Designation of copolymers used in this study



$$-\!\left(CH_2-\overset{R1}{\underset{R2}{C}}\right)_m\!-\!\left(CH_2-\overset{H}{\underset{OCCH_3 \atop \| \atop O}{C}}\right)_n\!-$$

Polymer code	Name of polymer	m (mol%)	n (mol%)	
			(R1=CH_3, R2=$COOCH_3$)	(R1=H, R2=1-pyrrolidone)
PMVC1	Poly(methyl methacrylate-co-vinyl acetate)	5.31	94.69	
PMVC2	Poly(methyl methacrylate-co-vinyl acetate)	10.30	89.70	–
PPVC	Poly(1-pyrrolidone-co-vinyl acetate)	49.80	–	50.20

Table 2. Designation of terpolymers having ethylene unit used in this study



$$-\!\left(CH_2-CH_2\right)_x\!\left(CH_2-\overset{H}{\underset{OCCH_3 \atop \| \atop O}{C}}\right)_y\!\left(A\right)_z\!-$$

Polymer code	Name of polymer	y (wt%)	z (wt%)	
			(A=carbon monoxide)	(A=maleic anhydride)
PEVACM1	Poly(ethylene-co-vinyl acetate-co-carbon monoxide)	24.00	10.00	–
PEVACM2	Poly(ethylene-co-vinyl acetate-co-carbon monoxide)	28.00	9.00	–
PEVAMA	Poly(ethylene-co-vinyl acetate)-graft-maleic anhydride)	18.00	–	0.62

Table 3. The composition of composite electrode [wt%]

Electrode	MCMB2528	$LiMn_2O_4$	Super-P carbon	PMVC1	Liquid electrolyte
Cathode	–	48.2	7.6	6.4	37.8
Anode	40.4	–	7.7	7.7	44.2

Table 4. Preparation recipe and ionic conductivity of gel polymer electrolytes

Gel electrolyte code	Polymer code	Gel composition (wt%)			Ionic conductivity (mS/cm)
		Polymer	Fumed silica	Liquid electrolyte*	
PMVC1G	PMVC1	20.0	20.0	60.0	1.36
PMVC2G	PMVC2	20.0	20.0	60.0	2.03
PPVCG	PPVC	15.0	25.0	60.0	0.89
PEVACM1G	PEVACM1	26.6	6.7	66.7	0.63
PEVACM2G	PEVACM2	26.6	6.7	66.7	0.75
PEVAMAG	PEVAMA	25.0	10.0	65.0	0.62

*1 M $LiClO_4$ in EC/PC (1 : 1 by vol.) was used as a liquid electrolyte.

main chains to examine the effect of fumed silica on ionic conductivity. Acrylic and ethylenic main chains are totally different in chemical features, especially in their affinity for carbonate-based solvents. We considered that there might be a synergetic effect to increasing ionic conductivity by incorporating vinyl acetate into acrylic homopolymer, and the phase separation problem between polymer matrix and carbonate-based solvent could be reduced by replacing polyethylene with ethylene/vinyl acetate copolymer.

Table 4 shows the result of ionic conductivity of gel polymer electrolytes prepared by using the copolymers listed in Table 2 and 3. All of the gel polymer electrolytes in Table 4 show good ionic conductivity over 0.5 mS/cm that is acceptable value to be used in lithium polymer batteries. They were all freestanding and had somewhat the elastic property without the exudation problem of liquid electrolyte.

Fumed silica itself is a blocking substance against the transport of lithium ion, but the addition of fumed silica gives positive effects to a gel polymer electrolyte. S. R. Raghavan *et al.* reported the effect of the addition of silica as follows: 1) enhancement of mechanical properties, 2) a superior interfacial stability for the electrolyte in contact with lithium metal, 3) increased ionic conductivity, 4) decreased level of polymer crystallinity.[14] D. W. Kim *et al.* introduced the absorption property of fumed silica that could hold liquid electrolyte.[15]

Figure 1 shows the effect of the content of fumed silica on the ionic conductivity of PMVC1 gel polymer electrolyte. The solubility of poly(methyl methacrylate) (PMMA) was increased by copolymerizing vinyl acetate moiety, but its gel polymer electrolyte was stickier than the gel polymer electrolyte prepared by using PMMA homopolymer. The increment of sticky property is correlated with the lower mechanical strength. PMVC1 gel polymer electrolyte could not be prepared unless fumed silica was added. It was thought that the addition of fumed silica could reinforce PMVC1 gel polymer electrolyte and more than 0.7 of the content of fumed silica was effective. The role of fumed silica in PMVC1G was the enhancement of mechanical properties.

The addition of fumed silica had, however, a different outcome in the case of PEVACM1. PEVACM1 gel polymer electrolyte still showed the freestanding property and enough mechanical strength even though vinyl acetate was incorporated. There was, however, the leakage problem of liquid electrolytes due to the phase separation between PEVACM1 and carbonate-based liquid electrolyte. Since the impedance pattern of PEVACM1 gel polymer electrolyte without fumed silica was so unstable due to the gradual leakage of liquid electrolyte, the reproducible value of the ionic conductivity

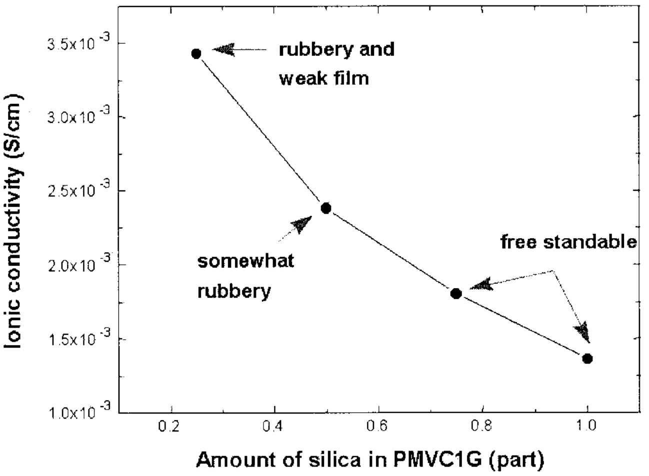


Figure 1. Correlation between ionic conductivity and apparent mechanical property with the content of fumed silica. The composition ratio of PMVC1/silica/1M $LiClO_4$ in EC/PC is 1/x/3 part (x denotes the amount of silica in PMVC1G).

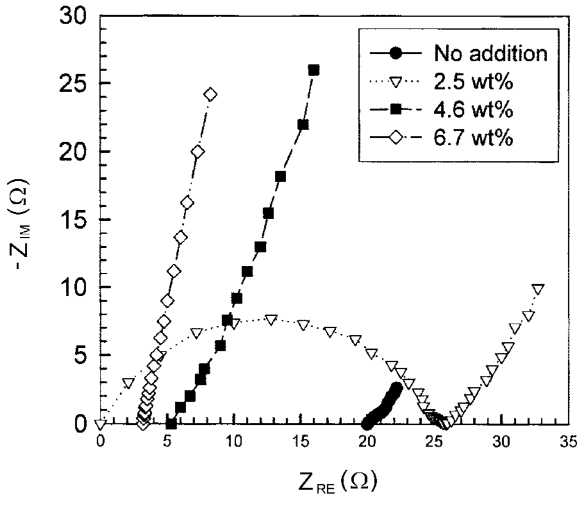


Figure 2. Various impedance patterns of PEVACM1 according to the fumed silica content measured at room temperature. The thinckness of PEVACM1 was 80 mm.

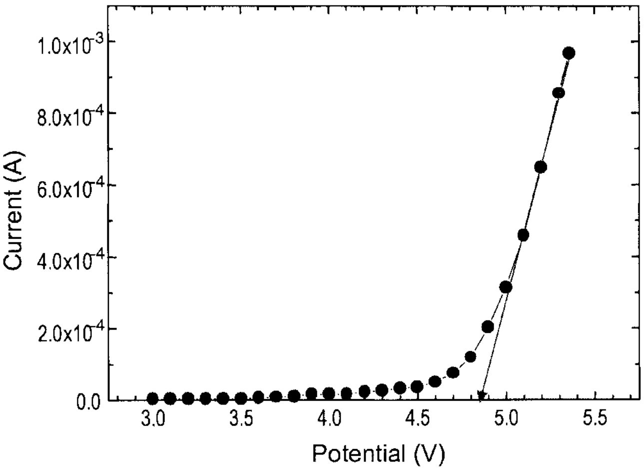


Figure 3. Electrochemical stability window of PMVC1G obtained by linear sweep voltammetry. (sweep rate = 1 mV/s).

could not be measured. In this case, adding fumed silica could reduce the exudation problem of liquid electrolyte from PEVACM1G as it absorbed carbonate-based solvents.

Linear sweep voltammetry test of PMVC1G. The electrochemical stability window for PMVC1G was examined and the result is shown in Figure 3. One of the important properties of gel polymer electrolyte for lithium polymer battery application is the voltage limitation of its electrochemical stability window. If the common intercalation material like lithium metal oxide is used as an active material for cathode, gel polymer electrolyte must have a stability window over 4.5 V (*vs*. Li metal). As shown in Fig. 3, PMVC1G displays stability over 4.8 V.

Charge/discharge performance of lithium polymer cell with PMVC1G. To check the applicability of PMVC1G in lithium ionic type polymer battery, we fabricated MCMB2528 composite anode/PMVC1G/$LiMn_2O_4$ composite cathode cell. Figure 4 shows the charge/discharge curves according to the cycle for the cell at a constant current density of 0.1 mA/cm^2 (0.2 C-rate). We found no significant decay of discharge capacity with the cycle. The specific discharge capacity was more than 110 mAh/g after the 50th charge/discharge test. It is concluded that PMVC1G gives a good lithium ionic conduction path and interfacial contact to the electrodes, which means no interfacial problem with the cycle.

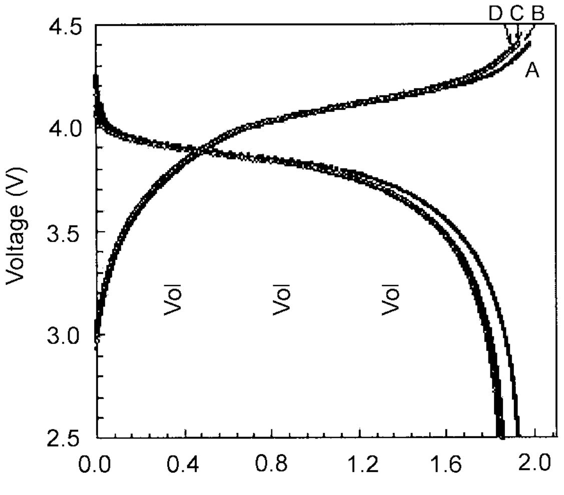


Figure 4. 0.2C-rate charge-discharge profile of lithium ionic type polymer cell with PMVC1G according to cycle number (A: formation (1/20C), B: 10th cycle, C: 25th cycle and D: 50th cycle).

Conclusions

We prepared two series of gel polymer electrolytes with poly(vinyl acetate) copolymers and examined the effect of the addition of fumed silica on the ionic conductivity. The addition of fumed silica in PMMA-based gel polymer electrolytes compensated for the lowering of the mechanical strength of poly(methyl methacrylate-co- vinyl acetate) gel polymer electrolyte resulted from the incorporation of vinyl acetate. In the case of ethylenic copolymers, the role of fumed silica was to alleviate the phase separation between ethylenic moiety and carbonate-based solvent. That means the embodiment of stable ionic conductivity over 0.5 mS/cm by introducing vinyl acetate could be achieved with the addition of fumed silica.

The charge/discharge performance of MCMB2528 composite anode/PMVC1G/ $LiMn_2O_4$ composite cathode cell gave promising results. We concluded that vinyl acetate moiety could reduce the interfacial resistance between PMVC1G and electrodes due to its good adhesion property. We will study the application of PMVC1G in $LiCoO_2$ and MCF electrode system that are widely used in commercial lithium secondary batteries. Poly(ethylene-co-vinyl acetate) copolymers are commercially available and very cheap. They can be strong candidates as polymer materials for gel polymer electrolyte provided its electrochemical performance is more improved.

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