

## Poly(vinyl alcohol) based Solid Polymer Electrolyte with Fast Cationic Transport Process

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### Introduction

Solid polymer electrolytes (SPEs) have been studied during the past two decades because they are the non-volatility, low toxicity, and higher energy density. Due to poor conductivity of SPEs at ambient temperature, however, several modification procedures have been investigated. Most modification procedures are investigations of amorphous polymer systems with alkali metal salts as the conduction species. In these systems, ion transport has mostly been associated with the segmental motion of the polymer, so significant conductivity is only observed above the glass transition temperature ( $T_g$ ) [1]. Namely, these kinds of SPEs are not entirely free from the drawback of lower ionic conductivity than gel polymer electrolytes (GPEs) at room temperature.

In this study, 'new type SPEs' having the ion transport mechanism decoupled from segmental motion of polymer based on poly (vinyl alcohol) (PVA) containing the salt of lithium trifluoromethanesulfonate ( $\text{LiCF}_3\text{SO}_3$ ) which shows remarkable chemical and electrochemical stability[2] have been prepared to overcome low ionic conductivity of 'traditional SPE' at room temperature. PVA has high glass transition temperature ( $T_g$ ) (358K) and good mechanical properties. So, these two components can be used to observe the electrochemical properties of SPEs with different salt concentrations and the mechanism of 'decoupled ion transportation', too.

### Experimental

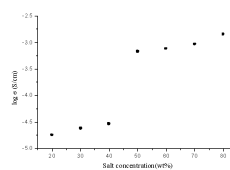
PVA (polymerization degree 1500, Yakuri pure chem. co.) was first dissolved in dimethylsulfoxide (DMSO) (Junsei chem. co.) and stirred overnight. Then, calculated amount of  $\text{LiCF}_3\text{SO}_3$  (Aldrich) was added to the polymer solution and stirred again overnight. The solution was cast on a stainless steel plate and allowed to dry under vacuum for various drying times at 40 °C. The stainless steel plate was to directly serve as the electrode in our conductivity cell.

The electrochemical properties of SPEs were studied by using linear sweep voltammetry (LSV, Zahner Electric IM6) and ac impedance analyzer (Zahner Electric IM6) over the frequency range 100mHz to 100kHz. The contribution of 'ion aggregates' was confirmed by atomic force microscopy (AFM) controlled by the Nanoscope IIIa scanning probe microscope controller with a Nanoscope Extender. Infrared absorption spectra were recorded by Jasco 460 Plus FT-IR spectrometer in the range of 4000 and 400  $\text{cm}^{-1}$ .

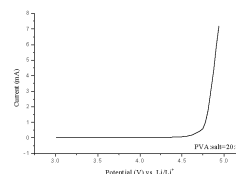
### Results and discussion

**The electrochemical properties.** Fig.1 presents the ionic conductivities of PVA/ $\text{LiCF}_3\text{SO}_3$  complexes as a function of salt concentration between 20 and 80 wt% at room temperature. The maximum conductivity ( $1.42 \times 10^{-3} \text{S/cm}$ ) is observed at room temperature for the highest salt concentration. And, a steady increase in conductivity is observed with increasing salt composition so the SPEs do not show the free volume behavior expected from a transport mechanism dependent on the polymer segmental motion, as many other polymeric system show. In addition, the ionic conductivity increased dramatically between 40 and 50wt% of salt concentration. Therefore we could know that with the change of the cation transport mechanism, efficient 'fast cationic transport process' was formed.

Fig. 2 illustrates the current-voltage response obtained from PVA- $\text{LiCF}_3\text{SO}_3$  complexes at the scan rate of 1mV/s. The decomposition of all polymer electrolytes begins beyond 4.0 except the SPE containing 20wt% of salts. And over than 50wt% of salt concentration, the electrochemical stabilities of PVA-  $\text{LiCF}_3\text{SO}_3$  complexes were markedly improved and sufficient for use in the lithium ion polymer battery. From these results, we could know that SPEs containing 'fast cationic transport process' had good electrochemical stabilities.



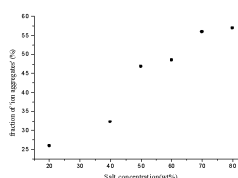
**Fig. 1.** Salt concentration dependence of the ionic conductivity of SPEs.



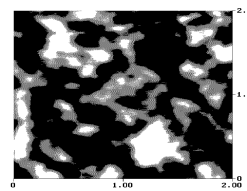
**Fig. 2.** LSV of the SPE (PVA:salt=20:80). Scan rate: 1mV/s.

**Ion aggregates.** Using the peak fitting results for all salt concentrations, we could obtain the fraction of each salt form and showed in Fig. 3. In Fig. 3, we could realize two interesting results. The first one is that the fraction of 'free ion' decreased with increasing salt concentration, on the other hand, the fraction of 'ion aggregates' increased. And the second one is that the increasing rate of ion aggregates fraction between 40 and 50wt% of salt concentrations was the largest one in all salt concentrations. We already know that ion conductivity increased dramatically between 40 and 50wt% of salt concentration same as the fraction of 'ion aggregates'. This suggests that the 'ion aggregates' have something to do with the 'fast cationic transport process'.

To confirm the contribution of 'ion aggregates' to the formation of 'fast cationic transport process', we decided to observe the arrangement of 'ion aggregates' in SPEs with various salt concentrations using AFM. It could be known that a number of large ion aggregates were formed and connected mutually like a network in the whole SPE films. The AFM image of the SPE with 50wt% of salt concentration was shown in Fig. 4. This connected large ion aggregates constitutes the 'fast cationic transport process' and in this 'fast cationic transport process' cations can move efficiently decoupled from polymer segmental mobility. As a result of this phenomenon, ionic conductivity increases rapidly. At more than 50wt% of salt concentration, there are a lot of small ion aggregates and ion pairs inside the ion aggregate network because of excess salts and we cannot distinguish the salt part from the polymer matrix.



**Fig. 3.** Fraction of ion aggregates as a function of salt concentration for PVA- $\text{LiCF}_3\text{SO}_3$  complexes.



**Fig. 4.** AFM image of PVA- $\text{LiCF}_3\text{SO}_3$  complex (2  $\mu\text{m} \times 2 \mu\text{m}$ ): PVA:salt=50:50.

### Conclusions

PVA-based SPEs have been prepared by solvent casting and evaluated using ac impedance, LSV, FTIR and AFM. Prepared SPEs showed a steady increase in ionic conductivity with increasing salt composition and the maximum conductivity ( $1.42 \times 10^{-3} \text{S/cm}$ ) was observed at room temperature for the highest salt concentration. From FT-IR and AFM results, we confirmed the formation of 'fast cationic transport process' at around 50wt% of salt concentration and observed the arrangement of ion aggregates in SPEs with small and large amount of salts. From above results, we could describe how Li cations move in PVA/ $\text{LiCF}_3\text{SO}_3$  SPEs at different salt concentrations. Over than 50wt% of salt concentration, Li ion can move by ion hopping in the effective 'fast cationic transport process' consisted of network-like connected large ion aggregates decoupled from polymer segmental motion. These new type PVA-based SPEs showed proper electrochemical stabilities for use in the lithium ion polymer battery.

### References

- [1] Gray F. M., Solid Polymer Electrolytes, VCH Publishers Inc., New York, (1991).
- [2] Davidson, M. G., Raithby, P. R., Johnson, A. L., Bolton, P. D., Eur. J. Inorg. Chem., 3445 (2003).