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Anion-Conducting Film Composed of Poly(vinyl chloride), Quarternary Ammonium Iodide, and Organotin Compound

Tatsuo FUJINAMI,* Hitoshi ISHIKAWA, Hiromitsu TAKAOKA,
Shin-ichi FUKUZAWA, Shizuyoshi SAKAI, and Masami OGITA†
Department of Materials Science, Faculty of Engineering,
Shizuoka University, Hamamatsu 432
†Junior College of Engineering, Shizuoka University, Hamamatsu 432

Anionic conductivity of poly(vinyl chloride)-tetrabutylammonium iodide composite film has been remarkably increased by the addition of organotin compounds. At a high content of tributyltin iodide, the conductivity has been enhanced up to the order of 10^{-4} S/cm at 25 °C.

Polymeric solid electrolytes are now the topic in the area of electrochemistry for applications to batteries, sensors, or electrochromic devices.[1] Cation conductors such as poly(ethylene oxide) complexes of lithium salts have been attracted much attention for use in all-solid-state batteries. Polymeric quaternary ammonium salts are familiar polyelectrolytes but their anionic conductivities in solid state are very low. It has been reported that ionic conductivities of polymeric ammonium chlorides depend on humidity[2] and are increased by addition of poly(ethylene glycol).[3] We wish report here the high anionic conductivities of films composed of poly(vinyl chloride) (PVC), tetrabutylammonium iodide (TBAI), and organotin compounds.

Transparent films were obtained by casting from the THF/methanol (4/1) solutions of PVC, TBAI, and organotin compounds, and their ionic conductivities (σ) were determined by AC impedance measurements under dry nitrogen atmosphere at 25 °C. Results are summarized in Table 1. TBAI-PVC film has a very low ionic conductivity presumably due to tight ion pairing in TBAI and restricted mobility of iodide ion in the rigid film. Plasticizers are well known to increase the segmental motion of polymer chain, but the addition of a plasticizer, dioctyl phthalate (DOP), to TBAI-PVC film resulted in a slight increase of the conductivity at room temperature. We found that the addition of organotin compounds significantly increased the anionic conductivity of TBAI-PVC film, and the degree of the increase was dependent on the chemical structures of organotin additives.

Organotin halides are Lewis acids whose acidities decrease in order of increase of alkyl groups attached to a tin atom.[4] The Lewis acidic tin atom is able to interact with iodide ion to form a five- or six-coordinated stannate complex. Therefore, the organotin compounds would be expected to reduce the ion pairing in TBAI salts and promote the anion transport in polymeric films.

Bu_4Sn is a very weak acid and can not interact with the anion satisfactory.

Table 1. Ionic conductivities of TBAI-organotin compound-PVC composite films at 25 °C[a)]

Organotin compound	log δ (S/cm)
none	-11 (-9.7)[b)]
Me_2SnI_2	- 7.7
Bu_2SnI_2	- 5.9
Bu_3SnI	- 4.9
Bu_4Sn	- 9.6
$(n\text{-}C_8H_{17})_2SnI_2$	- 5.1
$(n\text{-}C_8H_{17})_3SnI$	- 8.1
$(IBu_2Sn)_2O$	- 8.0
$(Bu_3Sn)_2O$	- 8.6

a) Weight ratio of TBAI / PVC is 1 / 2 and the ratio of Sn / N^+ is 2 / 1.
b) TBAI-DOP-PVC film (weight ratio 1 / 0.7 / 2).

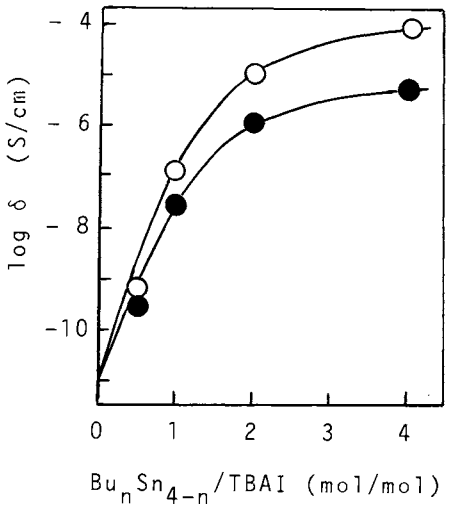

Fig. 1. Relationships between log δ and content of organotin compounds in TBAI-PVC film (weight ratio 1 / 2) at 25 °C. (○) Bu_3SnI, (●) Bu_2SnI_2

Even more acidic Me_2SnI_2 and Bu_2SnI_2 are less operative than Bu_3SnI. As expected, trioctyltin iodide is less effective than dioctyltin diiodide because of too large alkyl substituents. Since the bis(organotin) compounds are bidentate Lewis acids and tightly coordinated by iodide ion, they would tend to trap the mobile anion and were caused of lower conductivities than mono(organotin) iodides. These results demonstrate that loose binding of iodide ion to a tin atom with moderate Lewis acidity is favorable for the anion conduction which appears to be induced by migration of iodide ion from one to another tin atom through the coordination.

The ionic conductivity is improved as the content of organotin compounds (Fig. 1). In the wide range of the content, Bu_3SnI was more effective than Bu_2SnI_2. At the highest content of Bu_3SnI in Fig. 1, the conductivity increased up to the order of 10^{-4} S/cm at 25 °C.

References

1) M. B. Armand, J. M. Chabagno, and M. J. Duclot, "Fast Ion Transport in Solids," ed by P. Vashishta, J. N. Mundy, and G. K. Shenoy, North-Holland, New York (1979), p. 131; D. F. Shriver and G. C. Farrington, Chem. Eng. News, Nov. 25, p. 28 (1985); M. A. Ratner and D. F. Shriver, Chem. Rev., 88, 109 (1988), and other references cited therein.
2) Y. Sakai, Y. Sadaoka, and M. Matsuguchi, J. Electrochem. Soc., 136, 171 (1989), and references citen therein.
3) L. C. Hardy and D. F. Shriver, J. Am. Chem. Soc., 107, 3823 (1985).
4) R. C. Poller, "The Chemistry of Organotin Compounds," Logos Press, London (1970), p. 185.

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