PVDF-based polymeric gel electrolyte films for electrochemical devices

J. Tanimoto, M. Minami, T. Toya, S. Oshima,
T. Shinada, T. Kubo, and Y. Nishikitani

Central Technical Research Laboratory
Research & Development Division
NIPPON OIL CORPORATION
8, Chidoricho, Naka-ku, Yokohama, 231-0815 JAPAN

INTRODUCTION

Ionic conductors are essential constituent parts for electrochemical devices, batteries, electric double layer capacitors, electrochromic windows (ECWs), dye-sensitized solar cells, etc. These devices usually employ liquid electrolytes as the ionic conductors, the leakage from which inherently can reduce their long-term stability. To improve the stability, here we propose polymeric gel electrolyte films for electrochemical devices based on poly(vinylidene fluoride) (PVDF) derivatives. The polymeric gel electrolyte films so far obtained not only possess high tensile strength and good electrochemical stability, but also have high transparency, which is a necessary feature for ECW applications.

EXPERIMENTAL

Polymeric gel electrolyte films are composed of a PVDF-based matrix polymer, organic solvent (triethylphosphate (TEP) and/or tributylphosphate (TBP)) and a supporting electrolyte of lithium trifluoromethanesulfonate (LiOTF). A mixture of these three materials was coated on a poly(ethyleneterephthalate) film using a coating machine to form a thin, uniform electrolyte film. The film was then heat-treated to adjust the matrix polymer content of the electrolyte film. The matrix polymer content of the film was 45 mass% with 0.5 M of LiOTF in TEP and/or TBP. The content ratio of TEP to TBP was finely adjusted to vary the transparency of the film. The dimensions of the electrolyte film as prepared were from 100 to 200 μm in thickness and about 1000 mm in width. The ionic conductivity of the film was measured with an AC impedance method in the range between 30 and –30 degrees centigrade in a temperature-controlled chamber. The transparency of the electrolyte film was determined using a hazemeter with the electrolyte film sandwiched between two transparent glass substrates. The haze value is a measure of the transparency of an electrolyte film and is defined as the ratio of total light transmittance to diffusive transmittance [1].

RESULTS AND DISCUSSION

The temperature dependence of ionic conductivity (σ) of the 43 mass% matrix polymer electrolyte film is shown in Fig. 1; it scales well with the Vogel-Tamman-Fulcher (VTF) equation: $AT^{-0.5}\exp(-B/(T-T_0))$. The solid line in Fig. 1 is the best-fitted curve obtained with the VTF equation. The ionic conductivity of the electrolyte film at 25 degrees centigrade was as high as 10^{-4} S cm^{-1} without any diminishment in its freestanding property. Fig. 2 gives the haze values of the electrolyte films in four different LiOTF concentrations. The haze value decreases with the increase in the concentration of LiOTF, leveling off at about two per cent. Refractive index matching between the PVDF-based matrix polymer and the organic solvent is also a useful method to reduce the haze of the electrolyte film, or equivalently to increase the transparency.

In the presentation, the application of the electrolyte films to electrochemical devices will be also be discussed.

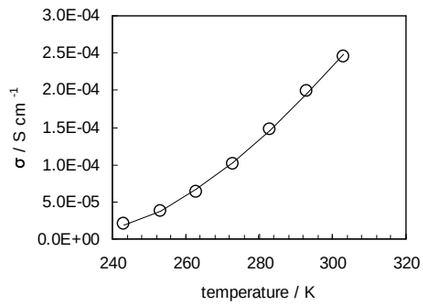

Fig. 1.
Ionic conductivity of a polymeric gel electrolyte film
(Matrix polymer: PVDF-HFP (polyvinylidene fluoride / hexafluoropropylene copolymer). Organic solvent: TEP/TBP. Supporting electrolyte: LiOTF.)

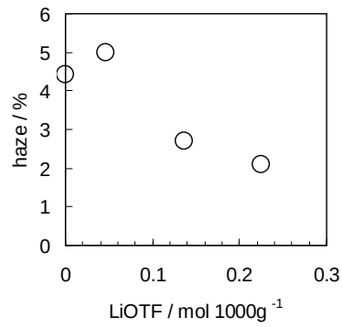

Fig. 2.
Haze of polymeric gel electrolyte films
(Matrix polymer: PVDF-HFP. Organic solvent: TEP. Supporting electrolyte: LiOTF.)

REFERENCE

1. ASTM D 1003: Standard Test Method for Haze Luminous Transmittance of Transparent Plastics