

## Proton Conducting Gel Electrolytes Based on Poly(ethylene oxide)-modified Polymethacrylate Doped with Inorganic Acids

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There have been many attempts to apply polymeric gel electrolyte systems to such electrochemical energy storage devices as batteries and capacitors. We have previously reported that a polymeric system consisting of poly(ethylene oxide)-modified polymethacrylate (PEO-PMA) with lithium salt is applicable to all-solid rechargeable lithium batteries owing to its high ionic conductivity as well as good chemical and mechanical properties (1). The PEO-PMA polymer matrix has high compatibility with not only lithium salts but also other inorganic salts with poly-valent cations (2). In this paper, we have examined the PEO-PMA-based gel system as a polymeric solid electrolyte conducting proton ( $H^+$ ) or hydroxide ( $OH^-$ ) ion at ambient temperature for electrochemical capacitor application.

Poly(ethylene oxide) monomethacrylate (PEM) and poly(ethylene oxide) dimethacrylate (PED) were used as prepolymers (macromers) for the matrix formation. Poly(ethylene glycol) dimethylether (PEGDE) as a plasticizer and 2,2-dimethoxy-2-phenylacetophenon as a photo-sensitizer were added into the mixed solution of the macromers. The resulting mixture was exposed to UV light to yield a cross-linked polymer matrix, PEO-PMA (Fig. 1). Then the prepared polymeric gel membranes were swollen in aqueous solutions of inorganic or organic electrolytes (HCl,  $H_3PO_4$ ,  $CH_3COOH$ , etc.) with various concentrations and immersion times. In this stage, the electrolytes were doped in the polymeric membranes, (PEO-PMA)/PEGDE/HX.

The ionic conductivity was measured by an AC method at an ambient temperature region (20 – 80 °C). The conductivity was dependent much on the sort of the doped electrolyte. It also varied with the electrolyte concentration, the immersion (swelling) time, and the plasticizer content. This type of proton conducting polymeric gels shares not only good mechanical properties but also high thermal stability. For the polymeric gel system doped with  $H_3PO_4$  as the electrolyte, (PEO-PMA)/PEGDE/ $H_3PO_4$ , maximum conductivities were  $2.6 \times 10^{-2} S cm^{-1}$  at 25°C and  $2.8 \times 10^{-2} S cm^{-1}$  at 70°C, where the composition of the polymer matrix to the plasticizer was 35/65 (in mass), after the  $H_3PO_4$  doping from the aqueous solution with  $2.93 mol dm^{-3}$ . FT-IR spectra showed that these high proton conductivities are attributed to the presence of excesses free  $H_3PO_4$  in the polymeric gel in addition to the hydrogen-bonded  $H_3PO_4$  to the polymer matrix.

The proton conductivity gave a good Arrhenius relation in the temperature range of 20 – 70 °C. The apparent activation energy for ionic conduction was generally lower than  $10 kJ mol^{-1}$ . Thus, both the Grotthus and Vehicle type mechanisms (3,4) exist in the conducting

process for the present (PEO-PMA)/PEGDE/ $H_3PO_4$ . That is, the ionic motion in the present gel system seems to be highly decoupled from the segmental motion of the polymer matrix, thus the conductivity is rather close to that of a liquid electrolyte system (5). Possible scheme is discussed for proton conduction in the present gel system. The PEO-PMA matrix is, in fact, plays a essential role to enclose the otherwise free phosphoric acid with a solid framework that provides a large number of charge carriers such as  $H_2PO_4^-$  and even  $H_4PO_4^+$ .

The conductance behavior of the systems doped with other electrolytes (HCl,  $CH_3COOH$ , etc.) was compared with that for  $H_3PO_4$ -doped system. The ionic conductivity of HCl-doped polymeric gel was rather instable, probably due to weak interaction between the polymeric matrix and incorporated acid. Lower conductivity was obtained for the gel system of (PEO-PMA)/PEGDE/ $CH_3COOH$ , in which lower degree of dissociation of the acid was suggested from the results of FT-IR experiments.

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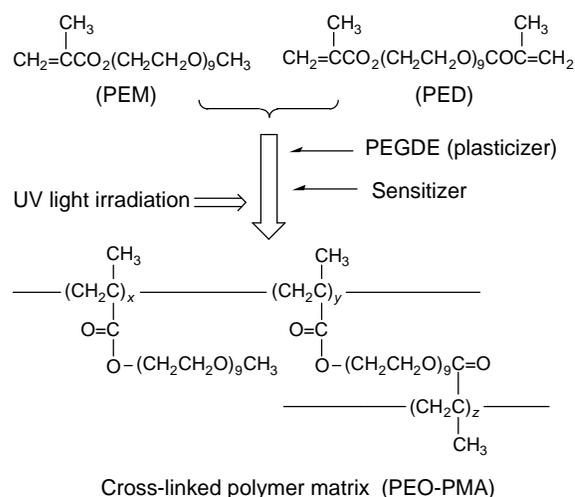


Fig. 1 A scheme for preparation of cross-linked polymer matrix with a plasticizer (PEGDE).