

Polymer 41 (2000) 8689-8696

polymer

www.elsevier.nl/locate/polymer

# Mechanical properties and ionic conductivities of plasticized polymer electrolytes based on ABS/PMMA blends

Xinping Hou, Kok Siong Siow $^*$ 

Department of Chemistry, The National University of Singapore, 3, Science Drive 3, Singapore, Singapore 117543

Received 15 November 1999; received in revised form 7 March 2000; accepted 31 March 2000

#### Abstract

A new plasticized polymer electrolyte composed of a blend of poly(acrylonitrile–butadiene–styrene) (ABS) and poly(methyl methacrylate) (PMMA) as a host polymer, mixture of ethylene carbonate (EC) and propylene carbonate (PC) as a plasticizer, and LiClO<sub>4</sub> as a salt was studied. Owing to the different miscibility of ABS and PMMA with the plasticizer, phase separation takes place in the electrolyte system as revealed from SEM studies. The ionic conductivity of the electrolytes decreased with the increasing ABS/PMMA ratio and increased with the increasing plasticizer content at the LiClO<sub>4</sub> content of 15%. Such conductivity behaviour could be explained in terms of the morphology and the thermal characteristics of the electrolytes. The mechanical property of the electrolytes was much improved compared with that of the electrolyte system containing pure PMMA, plasticizer and lithium salt. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer electrolytes; Dual-phase; Ionic conductivity

# 1. Introduction

In the past two decades, the progress of the portable consumer electronic devices has made it an urgent need to develop new design batteries with high energy density and long shelf life [1]. It is generally agreed that both these qualities can be achieved only by the lithium based electrochemical systems to configure the battery [2-6]. There are obvious drawbacks associated with the conventional nonaqueous organic liquid electrolytes like LiClO<sub>4</sub> in PC. Solid polymer electrolyte has been considered as an ideal alternative (to the liquid electrolyte counterpart) since its discovery by Armand et al. [7], and much work has been done to develop the practical all-solid state batteries based on solid polymer electrolytes (SPEs) [7-11]. A major disadvantage of SPEs, however, is the low ionic conductivity at ambient temperature, which is due to the low segmental mobility of the polymer chain complexed with lithium salt.

Various approaches have been attempted to improve the Li<sup>+</sup> ion mobility in the SPE matrix. These approaches include cross-linking two polymers [12,13], synthesizing new polymers [14,15], and adding plasticizers to polymer electrolytes to form plasticized polymer electrolytes (polymer gel electrolytes) [5,16–19]. The plasticizers used in

\* Corresponding author. Tel.: +65-8742923; fax: +65-7791691. *E-mail address:* chmsks@nus.edu.sg (K.S. Siow). plasticized polymer electrolytes are generally low molecular weight aprotic liquids having a low vapour pressure and high dielectric constant ( $\epsilon$ ), such as propylene carbonate (PC) ( $\epsilon = 64.4$ ) and ethylene carbonate (EC) ( $\epsilon = 89.6$ ). The role of a host polymer is secondary in this kind of electrolytes. The incorporated plasticizer imparts saltsolvating power and high ion mobility to the polymer electrolytes, which is necessary for ionic conduction [20]. The most important advantage of the plasticized electrolytes over the other polymer electrolytes is the relatively high ionic conductivity. However, such plasticized electrolytes are also known to have a number of important drawbacks, such as solvent volatility, poor mechanical property at high degree of plasticization, and reactivity of polar solvents with lithium electrode.

Poly(methyl methacrylate) (PMMA) is one of the host polymers commonly used in the plasticized polymer electrolytes [21,22]. The PMMA-based plasticized polymer electrolytes show high ionic conductivity of about  $1 \times 10^{-4}$  S cm<sup>-1</sup> at ambient temperature [21]. They could not, however, form free-standing films at high plasticizer content. One of the approaches to this problem is to blend PMMA with another polymer that can provide a good mechanical property [23].

We present in this paper our studies of a new plasticized polymer electrolyte system composed of ABS/PMMA blend as a host polymer, mixture of EC and PC (1:1 by

<sup>0032-3861/00/\$ -</sup> see front matter © 2000 Elsevier Science Ltd. All rights reserved. PII: \$0032-3861(00)00270-6

Table 1						
The compositon	and	appear	ance	of the	electrol	ytes

Samples	Polymer blend ratio (ABS/ PMMA)	Plasticizer content (%) <sup>a</sup>	Salt content (%) <sup>b</sup>	Appearance
AM73	7/3	0	0	Transparent film
AM64	6/4	0	0	Transparent film
PMMA	Pure PMMA	150	15	Transparent gel
AM1	2/8	150	15	Opaque gel
AM2	3/7	150	15	Opaque gel
AM3	4/6	150	15	Opaque gel
AM4	6/4	150	15	Opaque film
AM5	7/3	150	15	Opaque film
AM6	8/2	150	15	Opaque film
ABS	Pure ABS	150	15	Opaque film
AM7	6/4	50	15	Opaque film
AM8	6/4	100	15	Opaque film
AM9	6/4	200	15	Opaque film
AM10	6/4	250	15	Opaque gel
AM11	7/3	150	15	Opaque film
AM12	7/3	200	15	Opaque film
AM13	6/4	150	5	Opaque film
AM14	6/4	150	10	Opaque film
AM15	6/4	150	20	Opaque film
AM16	6/4	150	25	Opaque film
AM17	6/4	150	30	Opaque film

<sup>a</sup> Plasticizer content: (wt. plasticizer/wt. polymer) × 100%.

<sup>b</sup> Salt content: (wt. salt/wt. polymer)  $\times$  100%.

weight) as a plasticizer, and  $\text{LiClO}_4$  as a salt. ABS is used to improve the mechanical strength of the plasticized PMMA electrolyte system. The acrylonitrile unit in ABS is known to be able to interact with the plasticizer by ion–dipole interactions [24–26], while the butadiene and styrene units in ABS, which are immiscible with the plasticizer, can help to maintain the mechanical strength of the electrolytes. We have investigated the morphology and ionic conductivity as well as the mechanical strength of such plasticized polymer electrolytes.

## 2. Experimental

## 2.1. Materials

ABS with an average molecular weight of  $1.8 \times 10^5$  and a polydispersity of 2.18 was obtained from Polyscience Incorporation. PMMA with an average molecular weight of  $1.2 \times 10^5$  and polydispersity of 1.35 was obtained from Aldrich Chemical Company. Both the ABS and PMMA were precipitated with ethanol from tetrahydrofuran (THF) before use. High purity (99%) ethylene carbonate (EC) and propylene carbonate (PC) were purchased from Fluka and were used after distillation under reduced pressure. LiClO<sub>4</sub> (purity > 97%) was obtained from Fluka and was dried at 150°C under vacuum for 24 h before use. Tetrahydrofuran (THF) was purchased from J.T. Baker and was distilled with sodium before use.

## 2.2. Preparation of the electrolytes

All the electrolytes were prepared by the solution casting technique. The solutions were prepared by dissolving appropriate amounts of ABS, PMMA, EC/PC (1:1 by weight) and LiClO<sub>4</sub> in anhydrous THF. The solutions were then poured into a Teflon moulder and the solvent was allowed to evaporate at room temperature. Mechanically stable free-standing films (100-200µm) were obtained after the evaporation of the solvent. All the above operations were carried out in a dry box with N<sub>2</sub> flow. The films were then further dried in a temperature controlled vacuum oven at 50°C for 24 h to remove any trace of THF. In this paper, the plasticizer content is defined as: plasticizer content (%) = (weight of the incorporated plasticizer/weight of the total polymers) 100%; and the salt content as: salt content (%) = (weightof the incorporated salt/weight of the total polymers) 100%. The total polymer weights in all the electrolyte films are the same. The compositions of the prepared electrolytes are presented in Table 1.

## 2.3. Conductivity measurements

AC impedance and conductance measurements were performed over the frequency range of 100 KHz-1 Hz on an EG and G Model 273A Potentiostat/Galvanostat. A DT



Fig. 1. Scanning electron micrographs of the cross section of the host polymer blend (7/3) film (a) and the plasticized polymer electrolyte films with 15% LiClO<sub>4</sub>: (b) ABS/PMMA (7/3), 150% (EC + PC); (c) ABS/PMMA (6/4), 150% (EC + PC); (d) ABS/PMMA (6/4), 200% (EC + PC).

Hetotherm temperature controller was used to control the temperature of measurements. Samples for ionic conductivity measurements were prepared in a dry box filled with argon by sandwiching the polymer electrolyte films with two stainless steel disc electrodes of diameter 12.86 mm. Conductivity was calculated from the bulk resistance obtained from the impedance spectrum. Each sample was equilibrated at the experimental temperature for 30 min before measurement.

# 2.4. Morphology, mechanical strength and thermal analysis

Differential scanning calorimetry (DSC) measurements were carried out under nitrogen atmosphere with 2200 Thermal Analyser (Dupont) over the temperature range of -70to 150°C at a heating rate of 10°C min<sup>-1</sup>. Samples were sealed in aluminium pans in a dry box filled with argon. During the measurement, samples were quenched to -70°C and then heated to 150°C. The heat flow was recorded during the heating. Glass transition temperature ( $T_g$ ) was taken as the temperature of starting point of the baseline shift observed during the transition from glassy to rubbery state.

The morphology of the films was investigated by scanning electron microscopy (SEM) using a Philips XL30. Accelerating voltage was 10 kV. To prepare the samples for SEM, the plasticizer in the electrolyte films was removed by freeze drying without making any change to the morphology of the electrolytes. The samples for the SEM images of the cross section of films were then prepared by fracturing the films in liquid nitrogen.

The mechanical strength of the polymer electrolytes was measured from stress-strain tests using an Instron Model 5544 universal-testing instrument. The samples had been kept in a desiccator until the experiment, which lasted for about 1 min for each sample.

# 3. Results and discussion

#### 3.1. Morphology

The unplasticized films made of ABS/PMMA blend appeared transparent and exhibited only one glass transition temperature at ~70°C, showing that ABS was miscible with PMMA. However, the plasticized films prepared by casting the THF solution containing the mixture of EC/PC, LiClO<sub>4</sub> and ABS/PMMA had an opaque appearance. PMMA is miscible well with the EC/PC plasticizer. The opacity of the films could be attributed to the phase separation taking place due to the immiscibility of ABS, or more specifically, the butadiene and styrene units in ABS with the plasticizer and salt. The acrylonitrile unit in ABS is known to be miscible with the plasticizer and salt [5]. As is well known, the



Fig. 2. DSC curves of the polymer blend and the electrolyte film based on it. (a) ABS/PMMA(7/3); (b) ABS/PMMA(7/3), 100% (EC + PC), 15% LiClO<sub>4</sub>. Scan direction: -70 to 150°C.

salt in a gel polymer electrolyte is mainly dissolved in the plasticizer. From the viewpoint of materials study, we are concerned first with the optimal plasticiser concentration, and then with the concentration of salt that is compatible with the content of the plasticizer. Therefore, the effect of salt on the morphology is considered here together with that of the plasticizer.

Fig. 1 shows the SEM images of the cross section of the unplasticized film made of ABS/PMMA (7/3) blend and the cross section of the electrolyte films. It is clear that there is no phase separation in the unplasticized film. The film was prepared by the solution casting technique in the same way as for the electrolyte film preparation. On the other hand, there were pores on the cross section of the plasticized films. As ABS is not miscible well with the plasticizer, coagulation of the ABS may occur during the solution casting process. During this process, as THF is being evaporated and is getting decreased, ABS will begin to coagulate. When ABS coagulates completely, phase separation takes place as a result of reduced entropy and the morphology of the electrolyte is determined. The resulting film would then be composed of two phases: an ABS-rich phase and a plasticizer-rich phase. They provide the electrolytes with the



Fig. 3. Stress–strain curves of the electrolyte films. (a) ABS/PMMA(6/4), 150% (EC + PC), 15% LiClO<sub>4</sub>; (b) ABS/PMMA(6/4), 200% (EC + PC), 15% LiClO<sub>4</sub>; (c) ABS/PMMA(7/3), 150% (EC + PC), 15% LiClO<sub>4</sub>; (d) ABS/PMMA(7/3), 200% (EC + PC), 15% LiClO<sub>4</sub>.

mechanical strength and an ion path for electrolytes, respectively.

The rate of phase separation during casting depends on the composition of the cast solution. As the PMMA content in the solution is increased, the driving force for phase separation during film casting is reduced because PMMA is compatible with both the ABS and the plasticizer. The lower driving force for phase separation would reduce the rate of coagulation of ABS and therefore give rise to a better development of phase composed mainly of the plasticizer and the salt. High content of PMMA in the casting solution also gives rise to a larger plasticizer-rich phase after phase separation (refer to the SEM images in Fig. 1(c)), and hence a larger ionic path. This is similar to what has been observed in the PVC/PMMA system [23]. Both the ABS-rich phase and the plasticizer-rich phase contain PMMA because both ABS and plasticizer are miscible with PMMA.

Besides the PMMA content, the content of the plasticizer is also an important factor that would affect the phase separation rate of the electrolyte films. As the plasticizer content in the solution is changed, the distribution of PMMA, which is compatible with both ABS and plasticizer, would be different. Higher plasticizer content would allow more PMMA to be dissolved in the plasticizer-rich phase and therefore lead to a better development of the phase composed mainly of plasticizer and salt. As can be seen clearly in Fig. 1(d), even larger pores then appear in the SEM images of the cross section of the electrolytes.

The above explanation of phase separation was supported by the DSC results as shown in Fig. 2. For ABS/PMMA blend at 7/3 ratio, there was only one glass transition at about 70°C. However, for the plasticized electrolyte based on the same ABS/PMMA blend ratio, an obvious glass transition ( $T_{gl}$ ) at about 20°C appeared on the DSC curve. It is reasonable to assign  $T_{gl}$  to the plasticizer-rich phase formed by the miscibility of the plasticizer and PMMA. In addition, a second glass transition ( $T_{g2}$ ) appeared at about 50°C, which could be attributed to the ABS-rich phase.

## 3.2. Mechanical strength

The stress–strain testing results for several ABS/PMMA-EC/PC-LiClO<sub>4</sub> polymer electrolytes are presented in Fig. 3. The electrolyte with the ABS/PMMA blend ratio of 7/3 exhibited a critical stress of 6.6 MPa with an elongationat-break value of 98%. On the other hand, the electrolyte film with ABS/PMMA blend ratio of 6/4 showed a critical stress of 6.8 MPa (close to the value for the 7/3 electrolyte), but with a low elongation-at-break value at 30%. The reason that the electrolyte with the 7/3 polymer blend ratio was more elastic than the electrolyte with the 6/4 polymer blend ratio is that when there are more ABS in the electrolyte, more butadiene is available to provide the electrolyte with good elasticity. As both the electrolytes contain similar amounts of plasticizer, the effects of plasticizer on the mechanical strength of both electrolytes are limited to a



Fig. 4. The temperature dependence of the ionic conductivity for samples with 150% (EC + PC), 15%  $LiClO_4$  and different ABS/PMMA ratios. (a) pure PMMA; (b) ABS/PMMA = 2/8; (c) ABS/PMMA = 3/7; (d) ABS/PMMA = 4/6; (e) ABS/PMMA = 6/4; (f) ABS/PMMA = 7/3; (g) ABS/PMMA = 8/2; (h) pure ABS.

similar extent. The two electrolytes had therefore similar values of critical stress (6.6 and 6.8 MPa). However, when the plasticizer content was increased, both electrolytes showed a more drastic decrease in their elongation-atbreak values. Furthermore, when the plasticizer content

Table 2

Glass	transition	temperatures	$(T_g)$	and	the	inflection	temperatures	$(T_i)$
occurr	ed at the c	urves of log $\sigma$	$r \sim 1$	000 1	$\Gamma^{-1} f$	or the poly	mer electrolyt	es

PMMA,150%       17       20         (EC + PC), 15% LiClO <sub>4</sub> ABS/PMMA (2/8),       18       20 $150\%$ (EC + PC), 15%       LiClO <sub>4</sub> ABS/PMMA (3/7),       18       20 $150\%$ (EC + PC), 15%       LiClO <sub>4</sub> ABS/PMMA (3/7),       18       20 $150\%$ (EC + PC), 15%       LiClO <sub>4</sub> ABS/PMMA (4/6),       20       20 $150\%$ (EC + PC), 15%       LiClO <sub>4</sub> ABS/PMMA (4/6),       20       20 $150\%$ (EC + PC), 15%       LiClO <sub>4</sub> ABS/PMMA (6/4),       21       20
$\begin{array}{c} ({\rm EC} + {\rm PC}), 15\% \ {\rm LiClO_4} \\ {\rm ABS/PMMA} \ (2/8), & 18 & 20 \\ 150\% \ ({\rm EC} + {\rm PC}), 15\% \\ {\rm LiClO_4} \\ {\rm ABS/PMMA} \ (3/7), & 18 & 20 \\ 150\% \ ({\rm EC} + {\rm PC}), 15\% \\ {\rm LiClO_4} \\ {\rm ABS/PMMA} \ (4/6), & 20 & 20 \\ 150\% \ ({\rm EC} + {\rm PC}), 15\% \\ {\rm LiClO_4} \\ {\rm ABS/PMMA} \ (4/6), & 21 & 20 \end{array}$
ABS/PMMA (2/8), 18 20 150% (EC + PC), 15% LiClO <sub>4</sub> ABS/PMMA (3/7), 18 20 150% (EC + PC), 15% LiClO <sub>4</sub> ABS/PMMA (4/6), 20 20 150% (EC + PC), 15% LiClO <sub>4</sub> ABS/PMMA (6/4), 21 20
150% (EC + PC), 15% LiClO <sub>4</sub> ABS/PMMA (3/7), 18 20 150% (EC + PC), 15% LiClO <sub>4</sub> ABS/PMMA (4/6), 20 20 150% (EC + PC), 15% LiClO <sub>4</sub> ABS/PMMA (6/4), 21 20
LiClO <sub>4</sub> ABS/PMMA (3/7), 18 20 150% (EC + PC), 15% LiClO <sub>4</sub> ABS/PMMA (4/6), 20 20 150% (EC + PC), 15% LiClO <sub>4</sub> ABS/PMMA (6/4), 21 20
ABS/PMMA (3/7), 18 20 150% (EC + PC), 15% LiClO <sub>4</sub> ABS/PMMA (4/6), 20 20 150% (EC + PC), 15% LiClO <sub>4</sub> ABS/PMMA (6/4), 21 20
150% (EC + PC), 15% LiClO <sub>4</sub> ABS/PMMA (4/6), 20 20 150% (EC + PC), 15% LiClO <sub>4</sub> ABS/PMMA (6/4), 21 20
LiClO <sub>4</sub> ABS/PMMA (4/6), 20 20 150% (EC + PC), 15% LiClO <sub>4</sub> ABS/PMMA (6/4), 21 20
ABS/PMMA (4/6), 20 20 150% (EC + PC), 15% LiClO <sub>4</sub> ABS/PMMA (6/4), 21 20
150% (EC + PC), 15% LiClO <sub>4</sub> ABS/PMMA (6/4), 21 20
LiClO <sub>4</sub> ABS/PMMA (6/4), 21 20
ABS/PMMA (6/4), 21 20
1 FOR CERT BOX 1 FR
150% (EC + PC), $15%$
LiClO <sub>4</sub>
ABS/PMMA (7/3), 22 20
150% (EC + PC), 15%
LiClO <sub>4</sub>
ABS/PMMA (8/2), 24 25
150% (EC + PC), 15%
LiClO <sub>4</sub>
ABS, 150% (EC + PC), 28 30
15% LiClO <sub>4</sub>

was increased, there is also an obvious decrease in stress for the electrolyte with ABS/PMMA ratio of 6/4. These results are consistent with the morphology of electrolytes as revealed from the SEM images of their cross section (see Fig. 1(d)), which shows the presence of larger pores in the electrolyte with high content of plasticizer. In summary, the mechanical strength of the plasticized polymer electrolytes based on the ABS/PMMA blend depends on both the ratio of ABS/PMMA and the plasticizer content. For the polymer electrolyte with a fixed plasticiser content, especially a higher one, the ABS component has really improved the mechanical strength of the electrolyte.

## 3.3. Ionic conductivity

Ionic conductivity of the polymer electrolytes was evaluated by ac impedance with a symmetric cell, having the polymer electrolyte sandwiched between two stainless steel electrodes. We directly read the resistance of the electrolyte ( $R_b$ ) from the intercept of the impedance spectrum on the  $Z_{RE}$  axis considering the type of cell we studied here [27]. The conductivity ( $\sigma$ ) can then be calculated from

$$\sigma = \left(\frac{1}{R_{\rm b}}\right) \left(\frac{(L)}{A}\right) \tag{1}$$

where *L* is the thickness (cm) of the electrolyte film and *A* represents the electrode area (cm<sup>2</sup>).

Fig. 4 shows the temperature dependence of ionic conductivity in different ABS/PMMA blend ratio at the fixed plasticizer content of 150% and salt content of 15%. The conductivities at 20°C ranged from  $1 \times 10^{-5}$  to  $1 \times$  $10^{-3}$  S cm<sup>-1</sup>. The conductivity decreased with the increasing ratio of ABS/PMMA at the same temperature. Although the electrolyte with no ABS had the highest ionic conductivity values, it could not form a free-standing film and was in the form of a gel at room temperature. On the other hand, for the sample containing no PMMA, the room temperature conductivity value was found to be less than  $1 \times$  $10^{-5}$  S cm<sup>-1</sup>, which is two orders of magnitude lower than that of the sample containing no ABS, although it could form free-standing film with good mechanical strength. The films with the intermediate blend ratio of 6/ 4 and 7/3 showed good mechanical properties comparable with that containing no PMMA. However, their conductivities are slightly lower than those of the electrolytes with the ABS/PMMA blend ratio of 2/8, 3/7 and 4/6, which show gel-like mechanical properties at room temperature. For the electrolytes with a blend ratio of 6/4 and 7/3, the ABS-rich phase can support the electrolyte films effectively because of its solid-like medium, while the plasticizer-rich phase functions as a tunnel for ion transport to provide high ionic conductivity comparable with that containing no ABS. Owing to the blocking role of the ABS-rich phase, the ions have to move indirectly along a convoluted path, which could be responsible for the low conductivity at high ABS content. For the electrolyte with no ABS, the ions



Fig. 5. The temperature dependence of the ionic conductivity for samples with ABS/PMMA (6/4), 15%  $LiClO_4$  and different plasticizer content. (a) 50% (EC + PC); (b) 100% (EC + PC); (c) 150% (EC + PC); (d) 200% (EC + PC).

could move directly in a homogeneous conducting gel, which would be the reason for its relatively high ionic conductivity.

The plots in Fig. 4 show that inflections appear in all the plots around 20–30°C. The temperatures at which such inflection occurs ( $T_i$ ) correspond well with the glass transition temperatures of the respective electrolytes (see Table 2 for the  $T_g$  and  $T_i$  data). At temperatures below the inflection point, the electrolytes act as solid electrolytes and can be described by the classical Arrhenius theory. The temperature dependency of the conductivity ( $\sigma$ ) obeys the Arrhenius equation:

$$\sigma = K \exp \left[\frac{E_{a}}{RT}\right]$$
<sup>(2)</sup>

where *K* is a pre-exponential factor,  $E_a$  the activation energy and *T* the temperature in Kelvins. At temperature above the inflection point, the conduction behaviour follows the VTF equation that is applied widely to disorganised matter above  $T_g$  [28]:

$$\sigma = KT^{-0.5} \exp\left[\frac{-B}{(T-T_0)}\right]$$
(3)

where *B* is a pseudoactivation energy for ionic conduction, *K* a pre-exponential factor that is proportional to the number of charge carriers, and  $T_0$  (in Kelvins) a quasi-equilibrium glass transition temperature which has been reported to be  $30-50^{\circ}$ C lower than  $T_g$  for many polymer electrolyte systems [4].

Fig. 5 shows the Arrhenius plots for the ionic conductivity of the electrolytes containing ABS/PMMA blend ratio at 6/4 with a varying plasticizer content. The ionic conductivity increased with the increasing plasticizer content. This can be explained as being due to the increase in the volume fraction of the plasticizer-rich phase with increasing plasticizer content. The plasticizer-rich phase will then be less fragmented (or more interconnected), which makes ion transport easier.

It is interesting to note that the Arrhenius relation could be applied to the temperature dependency of the conductivity at low plasticizer content. At high plasticizer content, however, a slightly curved relation was observed indicating that the temperature dependency could be described by the VTF equation rather than by the Arrhenius equation. This behaviour is quite similar to that in the plasticized polymer electrolytes based on the PVC/PMMA blend [23]. At low plasticizer content, the volume of the plasticizer-rich phase is small and fragmented by the ABS-rich phase. The dissolved lithium ions would therefore transport mainly through the ABS-rich phase, which could be considered as a solid-like medium. In addition, the undissolved salt also forms some crystals in this situation. On the other hand, when the plasticizer is increased, the ions would transport mainly in the plasticizer-rich phase and the transport mechanism here could be governed by the free-volume related characteristic of the plasticizer-rich phase, which would be responsible for the VTF relation.

Fig. 6 shows the DSC heating curves for the ABS/PMMA (6/4) blend polymer electrolyte films with varying plasticizer content. It is clear that the glass transition temperatures of the electrolyte films decrease with the increasing plasticizer content. All films with plasticizer content less than 200% showed two glass transition temperatures corresponding to those for the plasticizer-rich phase and the ABS-rich phase, respectively. At low plasticizer content, e.g. 50% (EC + PC), the volume fraction of the ABS-rich phase is larger than that of the plasticizer-rich phase. As a result, there is a clear transition signal at about 50°C (for the ABS-rich phase) and a small transition signal at about 20°C (for the plasticizer-rich phase). With the increase of the plasticizer content, the plasticizer-rich phase dominates the thermal characteristics of the electrolytes with a very clear glass transition signal at about 20°C.

### 3.4. Electrochemical stability

For a lithium battery, the anodic reaction occurs in the vicinity of 0 V vs.  $\text{Li/Li}^+$  while the cathode potentials can approach as high as 4.5 V, implying that the electrochemical stability is also an important parameter regarding cycling reversibility. To evaluate the electrochemical stability of the ABS/PMMA based electrolytes, a three-electrode cell with stainless steel as the working electrode and lithium as counter and reference electrodes was assembled and its cyclic voltammetry measured. Fig. 7 illustrates the cyclic current-potential curves of the plasticized polymer electrolyte studied. With the decomposition potential being defined as



Fig. 6. DSC curves of the electrolytes with ABS/PMMA (6/4), 15% LiClO<sub>4</sub> and different plasticizer content. (a) 50% (EC + PC); (b) 100% (EC + PC); (c) 150% (EC + PC); (d) 200% (EC + PC). Scan direction:  $-70^{\circ}$ C to 150°C.

the potential at which the current density approaches  $0.1 \text{ mA cm}^{-2}$  [29], Fig. 7 indicates that the plasticized polymer electrolyte based on ABS/PMMA is electrochemically stable up to 4.5 V.

# 4. Conclusions

Plasticized dual-phase polymer electrolytes that possess good mechanical strength and high ionic conductivity were obtained by controlling the blend ratio of ABS and PMMA, the plasticizer and LiClO<sub>4</sub> content. The ionic conductivity



Fig. 7. Cyclic voltammograms for ABS/PMMA-(EC + PC)-LiClO<sub>4</sub> at 10 mV s<sup>-1</sup> and 25°C on a stainless steel working electrode vs. lithium from 2.0 to 6.0 V.

and mechanical strength of the electrolytes depend on the amount of plasticiser and the ratio of ABS/PMMA when the LiClO<sub>4</sub> content is 15%. The temperature dependency of the conductivity can be related to the Arrhenius equation or the VTF equation depending on the plasticizer content that affects the morphology of the electrolytes. The SEM observation and DSC analysis show that a dual-phase structure was created in which the plasticizer-rich phase provided a path for the ion transport and the ABS-rich phase acted as a mechanically supportive matrix. The stress-strain curves show that desirable mechanical properties have been achieved for practical use because of the incorporation of ABS into the system. The electrochemical properties and the morphology of the electrolytes studied here have shed light on practical application of lithium batteries.

### Acknowledgements

The authors are grateful to the National University of Singapore for a research grant for this work.

#### References

- Appetecchi GB, Dautzenberg G, Scrosati B. J Electrochem Soc 1996;143:6.
- [2] Gozdz AS, Tarascon JM, Schmutz CN, Warren PC, Gebizlioglu OS, Shokoohi FK. 10th Annual Battery Conference on Advances and Applications, USA, 1995.
- [3] Jiang Z, Alamgir M, Abraham KM. J Electrochem Soc 1995;142:3333.
- [4] Gray FM. Solid polymer electrolytes. Weinheim: VCH, 1991.
- [5] Scrosati B, editor. Application of electroactive polymers. Amsterdam: North-Holland, 1993.
- [6] Gray FM. Polymer electrolytes. The Royal Society of Chemistry, 1997.
- [7] Armand M, Chabagno TM, Duclot M. Second International Meeting on Solid Electrolytes, St. Andrews, Scotland, Extended Abstract, 20– 22 September 1978.
- [8] Watanabe M, Itoh M, et al. Macromolecules 1987;20:569.
- [9] Rawsky GC, Fujinami Tatsuo, Shriver DF. Chem Mater 1994;6:2208.[10] Bruce P. Solid state electrochemistry. Cambridge: Cambridge University Press, 1995.

- [11] Deng Z, Xu Q, Zheng Y, Wang G. J Power Sources 1994;50:369.
- [12] Maccallum JR, Smith MJ, Vincent CA. Solid State Ionics 1982;11:307.
- [13] Wieczorek W, Florjanczyk Z, Stevens JR. Electrochim Acta 1995;40:2251.
- [14] Xu Q, Wan G. J Power Sources 1993;41:315.
- [15] Selvaraj II, Chaklanobis S, Chadrasekhar V. J Electrochem Soc 1995;142:366.
- [16] Nagasubramanian G, Attia AI, Halpert G. J Appl Electrochem 1994;24:298.
- [17] Tallworth PE, Greenbaum SG, Croce F, Slane S, Salomon M. Electrochim Acta 1995;40(13–14):2137.
- [18] Morales E, Acosta JL. Solid State Ionics 1997;96:99.
- [19] Abbrent S, Lindgren J, Tegenfeldt J, Wendsjo A. Electrochim Acta 1998;43(10–11):1185.

- [20] MacCallum JR, Vincent CA. Polymer electrolyte reviews. London and New York: Elsevier, 1987 (141pp.).
- [21] Bohnke O, Frand G, Rezrazi M, Rousselot C, Truche C. Solid State Ionics 1993;66:97.
- [22] Lee MH, Kim HJ, Kim E, Rhee SB, Moon MJ. Solid State Ionics 1996;85:91.
- [23] Rhoo HJ, Kim HT, Park JK, Huang TS. Electrochim Acta 1997;42(10):1571.
- [24] Wang Z, Huang B, Wang S, Xue R, Huang X, Chen L. J Electrochem Soc 1997;144(3):778.
- [25] Lee KH, Park JK, Kim WJ. J Polym Sci B: Polym Phys 1999;37:247.
- [26] Hou X, Siow KS, Gao Z. J Solid State Electrochem 1999;3:387.
- [27] Sung H, Wang Y, Wan C. J Electrochem Soc 1998;145(4):1207.
- [28] Baril D, Michot C, Armand M. Solid State Ionics 1997;94:35.
- [29] Ossola F, Pistoia G, Seeber R, Ugo P. Electrochim Acta 1988;33:47.