Conductivities of Room Temperature Molten Salts Containing $ZnCl_2$, Measured by a Computerized Direct Current Method

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The conductivities of the binary room-temperature molten salt (RTMS) systems $ZnCl_2$-N-n-butylpyridinium chloride (BPC), $ZnCl_2$-1-ethyl-3-methylimidazolium chloride (EMIC) and $ZnCl_2$-benzyltriethylammonium chloride (BTEAC) have been measured at different temperatures and compositions by a d.c. four-probes method. The conductivities of the three RTMS are in the order $ZnCl_2$-EMIC > $ZnCl_2$-BPC > $ZnCl_2$-BTEAC.

In $ZnCl_2$-BPC the conductivity at 70 to 150 °C, is maximal for 40 mol% $ZnCl_2$. In $ZnCl_2$-EMIC, the conductivity below 130 °C is almost constant for 30 to 50 mol% $ZnCl_2$ and has the lowest activation energy 25.21 kJ/mol. For these two systems, the conductivities decrease rapidly beyond 50 mol% $ZnCl_2$ owing to the rapid increase in cross-linking and resultant tightening of the polyelectrolyte structure. As to the $ZnCl_2$-BTEAC system, the conductivities at 110 - 150 °C decrease slowly for 30 - 60 mol% $ZnCl_2$. The conductivities of the $ZnCl_2$-EMIC melt are compared with those of the $AlCl_3$-EMIC melt previously studied.

The stability of the $ZnCl_2$-EMIC melt system is explored by the effect of the environment on the conductivity and the Far Transmission Infra Red (FTIR) spectrum. It reveals that the effect is slight, and that the $ZnCl_2$-EMIC melt may be classified as stable.

Key words: Conductivity; Room-temperature Molten Salt; $ZnCl_2$; Direct Current Method; Stable Melt.

Introduction

Molten salts possess some unique properties, e. g., high conductivity, a wide electrochemical window and low vapor pressure. Therefore molten salts are suitable electrolytes for the electrodeposition of metals. In recent years, molten salts have extensively been explored for their application as, e. g., electrodeposition electrolysis of metals, battery and fuel cell electrolytes, media for plating optical data storage materials, and melt catalysts for syntheses of new chemicals. Especially research on room temperature molten salts (RTMS) has drawn considerable attention. Hussey [1] has noted that industrial exploitation of RTMS looks extremely favorable. Unfortunately, however, conductivity data for RTMS are still scarce.

One of the most well known RTMS contains $AlCl_3$. We [2] have reported the conductivities of the three binary systems $AlCl_3$-BPC, $AlCl_3$-EMIC and $AlCl_3$-BTEAC by a computerized direct current method. $AlCl_3$ is a strong Lewis acid, so that the melts containing $AlCl_3$ are easily affected by the environment. This makes these melts often inconvenient for handling. Therefore more stable RTMS are wanted.

In the present study, the three systems $ZnCl_2$-BPC (N-n-butylpyridinium chloride), $ZnCl_2$-EMIC (1-ethyl-3-methylimidazolium chloride) and $ZnCl_2$-BTEAC (benzyltriethylammonium chloride) were selected for measurements of the conductivities. The $ZnCl_2$-BPC system was used in the electrodeposition of armorphous Co-Zn alloy from molten $CoCl_2$-$ZnCl_2$-BPC by Koura et al. [3]. In the literature, the conductivity of various ternary melts was reported, but the conductivity of the binary $ZnCl_2$-BPC was not presented. Sun et al. [4 - 6] studied on the electrodeposition of Zn, Co, Zn-Co and Zn-Cu alloys from the acidic $ZnCl_2$-EMIC melt. However the conductivity of $ZnCl_2$-EMIC melt was not reported. BPC and EMIC are hardly commercially available and therefore expensive, although they are needed as RTMS. BTEAC is commercially available and cheaper.

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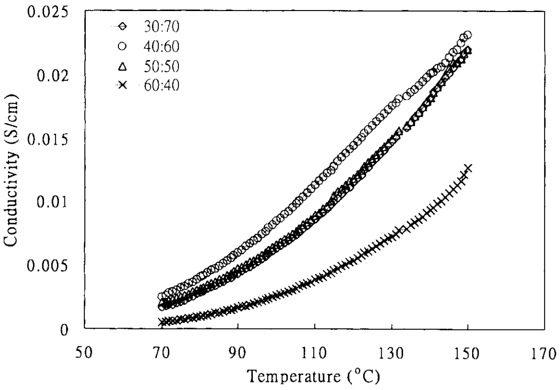

Fig. 1. The electrical conductivity of molten mixtures of $ZnCl_2$:BPC as a function of temperature. Composition in mol%: ◇, 30:70; ○, 40:60; △, 50:50; ×, 60:40.

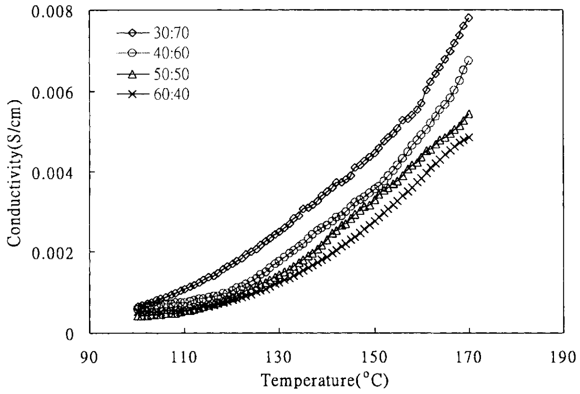

Fig. 3. The electrical conductivity of molten mixtures of $ZnCl_2$:BTEAC as a function of temperature. Composition in mol%: ◇, 30:70; ○, 40:60; △, 50:50; ×, 60:40.

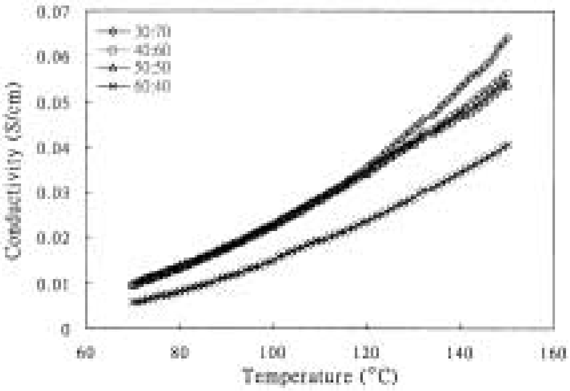

Fig. 2. The electrical conductivity of molten mixtures of $ZnCl_2$:EMIC as a function of temperature. Composition in mol%: ◇, 30:70; ○, 40:60; △, 50:50; ×, 60:40.

In this work, the conductivities of the three systems $ZnCl_2$-BPC, $ZnCl_2$-EMIC and $ZnCl_2$-BTEAC are reported for the first time. The conductivity of $ZnCl_2$-EMIC melt is compared with that of $AlCl_3$-EMIC melt. The effect of the environment on $ZnCl_2$-EMIC melt is explored by the conductivity measurement and Far Transmission Infra Red (FTIR) spectroscopy.

Experimental

$ZnCl_2$ (Merck, anhydrous, 98%), BPC (N-n-butylpyridinium chloride, TCI, 98%), EMIC (1-ethyl-3-methylimidazolium chloride, Aldrich, 98%) and BTEAC (benzyltriethylammonium chloride, Acros, 98%) were used as received. The molten salts with different molar ratios were prepared by continuous stirring for 12 hours under a purified nitrogen atmosphere in a glove box. The electrical conductivities of these melts were measured by the computerized measurement system for a d. c. four-probes method described in [2]. Pt electrodes were used, and the conductivities of the melts were measured under purified nitrogen. The furnace was controlled by a PID-Controller, the thermocouple of which measured the temperature in a silicon oil bath. The temperature of the melt near the voltage drop section was also measured by a thermocouple.

$ZnCl_2$-EMIC melt was used to explore the effect of the environment. The conductivity and FTIR spectra of this melt were measured soon after its preparation in a glove box and, after storing in a simple container after one day, three days and five days.

Results and Discussion

The conductivities of the binaries $ZnCl_2$-BPC, $ZnCl_2$-EMIC and $ZnCl_2$-BTEAC are shown as a function of temperature in Figs. 1, 2 and 3, respectively. The experimental data were least-squares fitted to equations of the form

$$\sigma = a + bt + ct^2, \tag{1}$$

where t is the temperature in °C. The obtained parameters a, b, and c are given in Tables 1, 2 and 3. As the R squared values are larger than 0.998, the above equations fit the experimental data very well. Figs. 1 and 2 show that the specific conductivities of the $ZnCl_2$-BPC and $ZnCl_2$-EMIC systems increase smothly with temperature, while this is not the case with the $ZnCl_2$-BTEAC system, as show in Figure 3.

Table 1. Parameters of (1) for $ZnCl_2$-BPC.

Melt comp.	$a\times10^3$	$b\times10^4$	$c\times10^6$	R squared	Temp. (°C)
30 mol% $ZnCl_2$	4.879	–1.880	2.02	0.99987	70 - 150
40 mol% $ZnCl_2$	–8.02	0.84	0.835	0.99766	70 - 150
50 mol% $ZnCl_2$	4.621	–1.741	1.943	0.99963	70 - 150
60 mol% $ZnCl_2$	7.156	–2.028	1.567	0.99874	70 - 150

Table 2. Parameters of (1) for $ZnCl_2$-EMIC.

Melt comp.	$a\times10^3$	$b\times10^4$	$c\times10^6$	R squared	Temp. (°C)
30 mol% $ZnCl_2$	140.3	–39.40	4.81	0.99954	70 - 150
40 mol% $ZnCl_2$	0.230	–6.826	2.951	0.99984	70 - 150
50 mol% $ZnCl_2$	–94.34	13.63	1.919	0.99934	70 - 150
60 mol% $ZnCl_2$	–0.936	–8.534	2.372	0.99979	70 - 150

Table 3. Parameters of (1) for $ZnCl_2$-BETAC.

Melt comp.	$a\times10^3$	$b\times10^4$	$c\times10^6$	R squared	Temp. (°C)
30 mol% $ZnCl_2$	7.963	–1.717	0.994	0.99723	100 - 170
40 mol% $ZnCl_2$	12.3	–2.345	1.179	0.9981	100 - 170
50 mol% $ZnCl_2$	7.616	–1.598	0.869	0.9975	100 - 170
60 mol% $ZnCl_2$	10.9	–2.03	0.988	0.9995	100 - 170

Table 4. Activation energies E_a (kJ/mol) from Arrhenius fits (2) of the conductivity data.

Melt composition	30:70	40:60	50:50	60:40
$ZnCl_2$-BPC	38.32	32.96	35.90	46.47
$ZnCl_2$-EMIC	28.09	25.99	25.21	29.13
$ZnCl_2$-BTEAC	46.78	49.97	55.29	49.91

These conductivities were fitted by the Arrhenius equation [7 - 10].

$$\sigma = \sigma_0 \exp\left[-\frac{E_a}{RT}\right]. \tag{2}$$

The data for the three melts are shown in Figs. 4, 5 and 6. These results reveal that the Arrhenius equation over the temperature range studied is quite well obeyed. The activation energies (E_a) are presented in Table 4 [9, 10]. They indicate that the $ZnCl_2$-EMIC melts have the lowest activation energy, the value being 25.21 kJ/mol for the 50:50 melt. This may be explained by the planarity and small lattice energy [11, 12], the planarity inherent in the imidazolium salt being assumed to promote the conductivity. Further, the lattice energy of the $ZnCl_2$-EMIC melt is lowest. The binary $ZnCl_2$-BTEAC melts have the highest activation energy, presumably because of the poor planarity and high lattice energy. Generally, a salt with a low lattice energy tends to possess a high ionic conductivity, because a low dissociation energy increases the number of free ions.

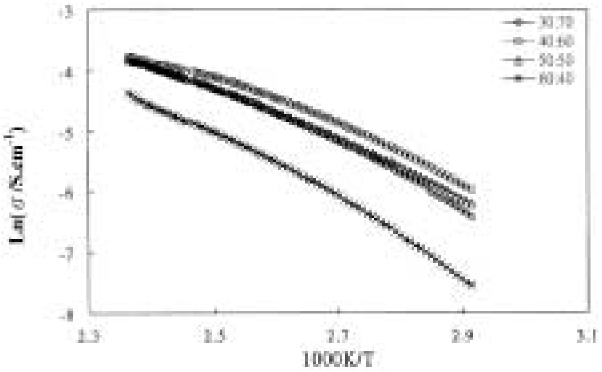

Fig. 4. Arrhenius plots of the electrical conductivity for molten mixture of $ZnCl_2$:BPC. Composition in mol%: ◇, 30:70; ○, 40:60; △, 50:50; ×, 60:40.

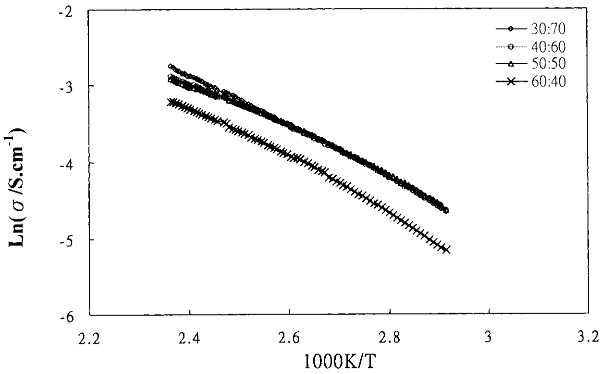

Fig. 5. Arrhenius plots of the electrical conductivity for molten mixture of $ZnCl_2$:EMIC. Composition in mol%: ◇, 30:70; ○, 40:60; △, 50:50; ×, 60:40.

The relationship between the conductivity and composition of the three systems at various temperatures is shown in Figs. 7, 8, and 9. Figure 7 shows that there is a maximum of the conductivity for 40 mol% $ZnCl_2$ at 70 to 150 °C. For $ZnCl_2$-BPC, neither the acid-base equilibria nor the conductivity have been reported. Easteal and Angell [13] have studied the phase equilibria and electrical conductance of $ZnCl_2$-pyridinium chloride (PC) melt. They indicate that the "ideal" glass transition temperature T_0 and the glass transition temperature T_g show a complex composition dependence. In addition, the phase equilibrium study of the system indicated the existence of four congruently melting compounds: R_4ZnCl_6, R_2ZnCl_4,

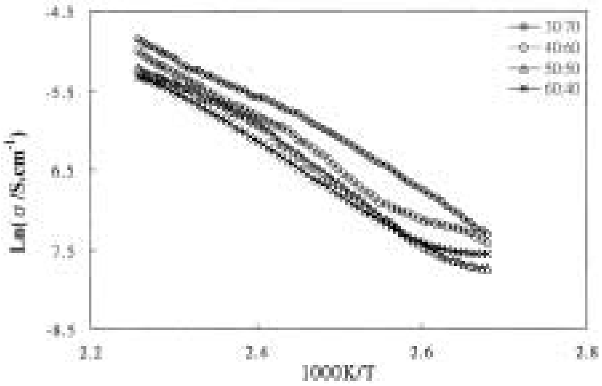

Fig. 6. Arrhenius plots of the electrical conductivity for molten mixture of $ZnCl_2$:BTEAC. Composition in mol%: ◇, 30:70; ○, 40:60; △, 50:50; ×, 60:40.

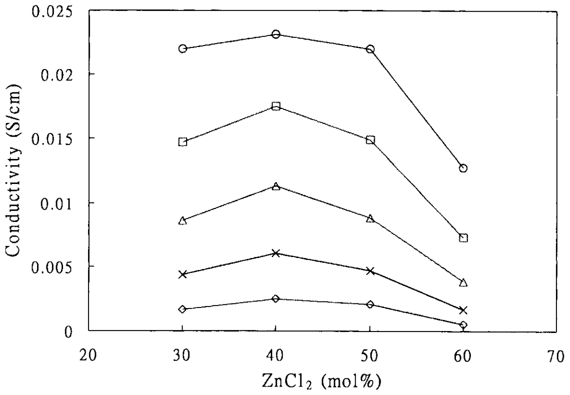

Fig. 7. The electrical conductivity of molten $ZnCl_2$-BPC as a function of the mol% of $ZnCl_2$ at different temperatures. ◇, 70 °C; ×, 90 °C; △, 110 °C; □, 130 °C; ○, 150 °C.

$RZnCl_3$, and RZn_2Cl_5 (R = pyridinium cation). On the $ZnCl_2$-rich side the chloride ion content is insufficient to satisfy individually the tetra-coordination required for the Zn^{2+} ions, forcing tetrahedral $ZnCl_4^-$ to share its corners with other ones in order to preserve the favored coordination number. This leads to the formation of $Zn_2Cl_7^{3-}$ structural groups at 40 mol% $ZnCl_2$, for which evidence has been presented in [14 - 16]. This also leads to increasingly long, and/or complex associations if the $ZnCl_2$ content increase beyond 40 mol%. Based on these phenomena, the conductivity of $ZnCl_2$-BPC decreases slowly at more than 40 mol% $ZnCl_2$. The decrease in the thermal expansivity beyond 50 mol% $ZnCl_2$ is consistent with a rapid increase in cross-linking and resultant tightening of the polyelectrolyte structure of $ZnCl_2$-PC [13].

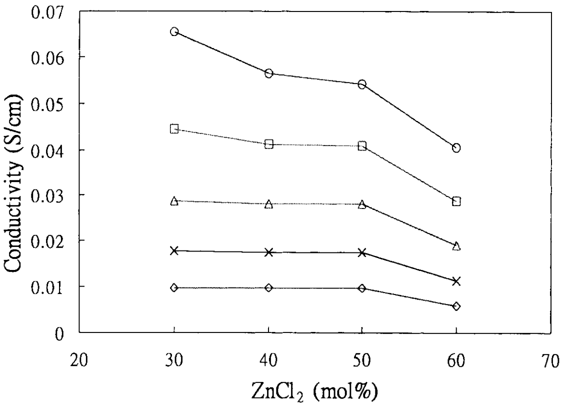

Fig. 8. The electrical conductivity of molten $ZnCl_2$-EMIC as a function of the mol% of $ZnCl_2$ at different temperatures. ◇, 70 °C; ×, 90 °C; △, 110 °C; □, 130 °C; ○, 150 °C.

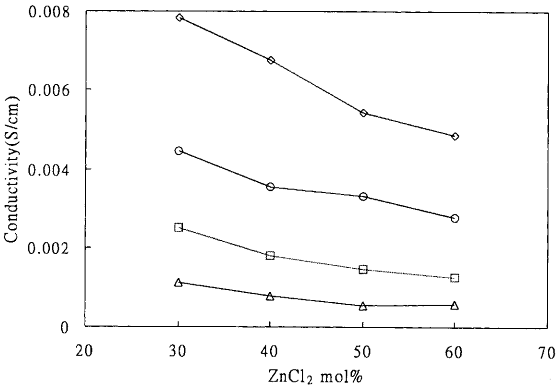

Fig. 9. The electrical conductivity of molten $ZnCl_2$-BTEAC as a function of the mol% of $ZnCl_2$ at different temperatures. △, 110 °C; □, 130 °C; ○, 150 °C.

It is assumed that $ZnCl_2$-BPC behaves similarly as the $ZnCl_2$-PC, the conductivity decreasing rapidly beyond 50 mol% $ZnCl_2$. Moreover, it is helpful to consult the literature data on $ZnCl_2$-MCl (M = alkali metal) systems [15, 17 - 19]. From the literature it can be assumed that the melts containing more than 33 mol% $ZnCl_2$ are acidic, owing to the presence of an excess amount of the Lewis-acidic $ZnCl_2$. Thus, there are not enough chloride ions to fully coordinate with Zn^{2+}, resulting in the zinc species $ZnCl_3^-$, $Zn_2Cl_7^{3-}$ and $(ZnCl_2)_n$, which are chloride ion acceptors. The melts that contain less than 33 mol% $ZnCl_2$ are assumed to be basic, because there is an excess amount of Lewis-basic chloride ions in the melts. In the basic melt, the major zinc species is

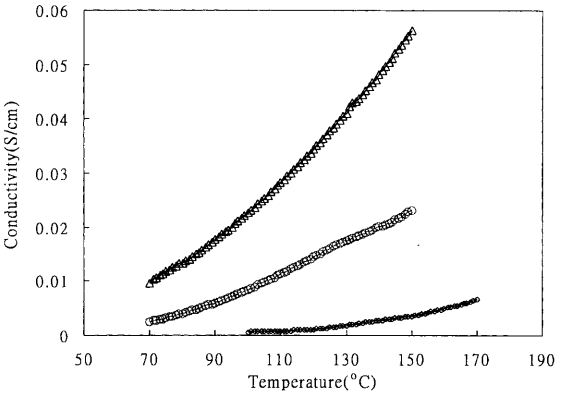

Fig. 10. Temperature dependence of the electrical conductivity of the three binary molten mixtures with $ZnCl_2$ 40 mol%. ○, $ZnCl_2$-BPC; △, $ZnCl_2$-EMIC; ◇, $ZnCl_2$-BTEAC.

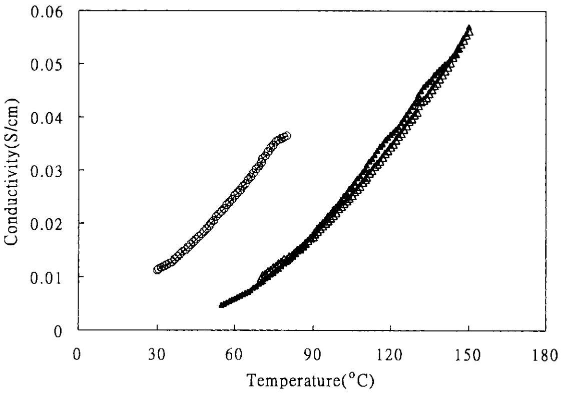

Fig. 11. Temperature dependence of the electrical conductivity of the two binary molten mixtures with EMIC 60 mol%. ○, $AlCl_3$-EMIC; △, $ZnCl_2$-EMIC.

presumably the monomeric $ZnCl_4^{2-}$ anion; however, the exact behavior of the melt needs to be verified by spectroscopy.

Figure 8 shows that, in the $ZnCl_2$-EMIC melt, the conductivity is almost constant at 30 to 50 mol% $ZnCl_2$, and that it considerably increases from 70 to 170 °C. The fact that the conductivity decreases beyond 50mol%$ZnCl_2$ is similar to the $ZnCl_2$-BPC system, owing to the considerable increase in cross-linking and resultant tightening of the polyelectrolyte structure. However, spectroscopic study is needed to obtain further information of the $ZnCl_2$-EMIC melt system.

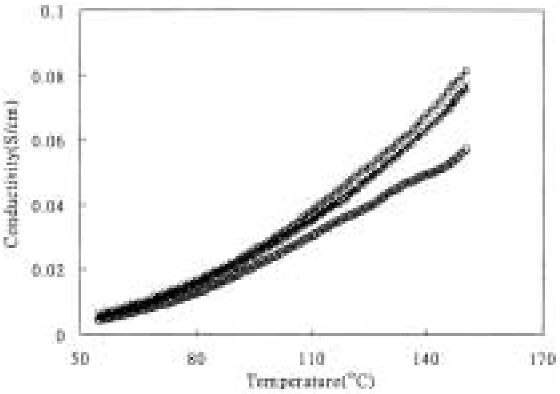

Fig. 12. The electrical conductivity of 40 mol% $ZnCl_2$:60 mol% EMIC melt as a function of temperature at various storage days. Storage days: ○, 0 day(instantly); ◇, 1 day; △, 3 days; □, 5 days.

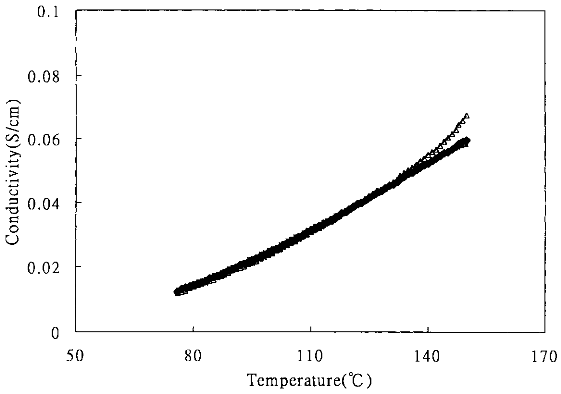

Fig. 13. The electrical conductivity of 50 mol% $ZnCl_2$:50 mol% EMIC melt as a function of temperature at various storage days. Storage days: ○, 0 day(instantly); ◇, 1 day; △, 3 days; □, 5 days.

Figure 9 shows that the conductivities at 110 - 170 °C, gradually decrease at 30 - 60 mol% $ZnCl_2$ and the values are about 0.001 to 0.008 S/cm which are smaller by one order of magnitude than those of the $ZnCl_2$-EMIC melt systems.

Figure 10 shows the electrical conductivities of the melts $ZnCl_2$-BPC, $ZnCl_2$-EMIC and $ZnCl_2$-BTEAC at 40% $ZnCl_2$ as a function of temperature. The $ZnCl_2$-EMIC melt has the largest slope of the conductivity as a function of temperature and clearly a higher conductivity than the other two melts have. The results may be explained in terms of the planarity and lower lattice energy. Moreover, the $ZnCl_2$-EMIC melt system also shows a remarkable increase in the conductivity as a function of the composition. As to the conductivities, $ZnCl_2$-EMIC > $ZnCl_2$-BPC > $ZnCl_2$-BTEAC.

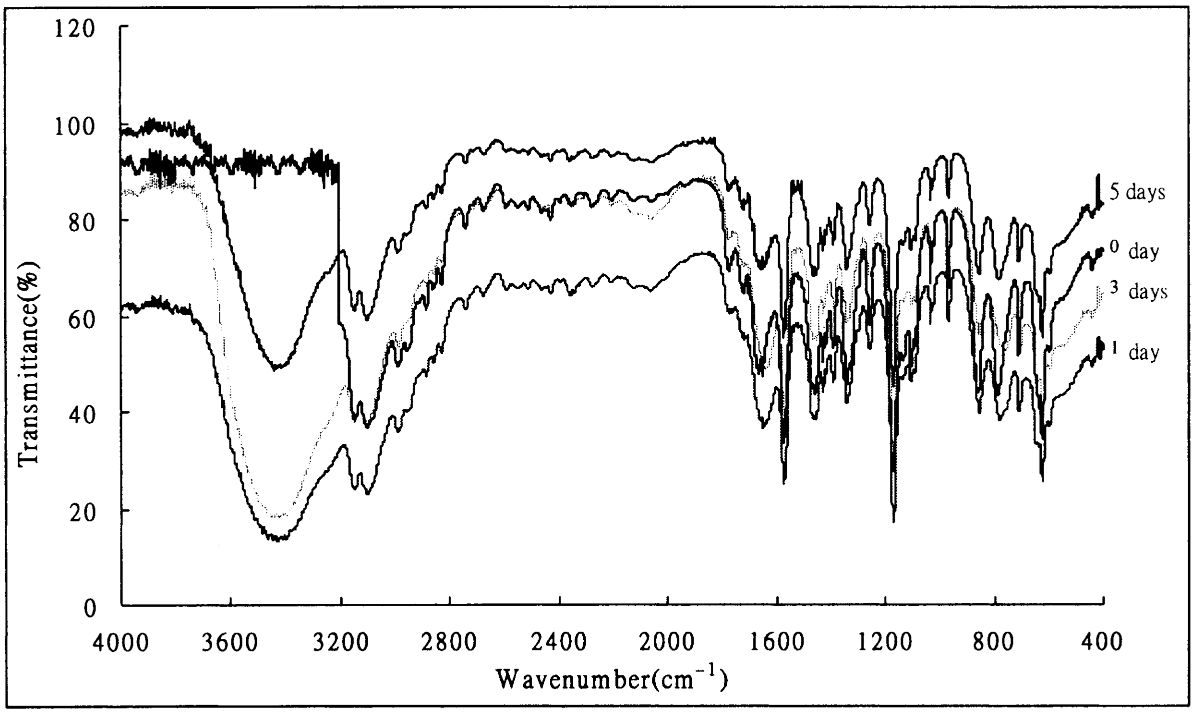

Fig. 14. The FTIR spectrum of 40 mol% $ZnCl_2$:60 mol% EMIC melt at various storage days.

In a previous paper [2], the conductivities of RTMS containing $AlCl_3$ have been concluded to be in the sequence $AlCl_3$-EMIC > $AlCl_3$-BPC > $AlCl_3$-BTEAC. Thus, binary melt system containing EMIC seem to have, in general, larger conductivities than those containing BPC and BTEAC, which may be attributed to the degree of planarity and the scale of lattice energy.

In Fig. 11 the conductivity in $ZnCl_2$-EMIC melt containing 60 mol% EMIC is compared with that of the corresponding binary $AlCl_3$-EMIC as a function of temperature, which indicates that the two melt systems have a similarity in a gradual increase in the conductivities with increasing temperature. Further, Fig. 11 also indicates that a higher temperature by about 40 °C is needed for the $ZnCl_2$-EMIC melt system to have comparable conductivity which that of the $AlCl_3$-EMIC, which has a higher conductive than the $ZnCl_2$-EMIC melt system. This is presumable because the $AlCl_4^-$ ion is species has a larger ionic mobility due to its monovalent ion in contrast to the divalent $ZnCl_4^{2-}$. In addition, $ZnCl_4$ is polymerized to some extent by corner sharing.

In the present study, the stability of the $ZnCl_2$-EMIC melt systems is explored by the effect of external environment on the conductivity and the FTIR spectrum. Figures 12 and 13 show that the conductivities of the $ZnCl_2$-EMIC melts, measured instantly after the melt prepared in a glove box and repeatedly after storing in a simple container for one day, three days and five days. Further, a spectroscopic analysis of the 40 mol% $ZnCl_2$ - 60mol% EMIC melt was carried out by FTIR after the conductivity measurement; the FTIR spectrum is shown in Figure 14. Figures 12 and 13 indicate that the effect of external environment on the $ZnCl_2$-EMIC melt is slight. The conductivity of the melt stored in a simple container for one day, three days and five days was similar but slightly higher than that of the newly prepared one. The slight increase may be explained in terms of the effect of moisture in the environment; the O-H stretching is observed as seen from Fig. 14, except for the spectrum of the newly prepared sample. Further, Fig. 14 reveals that these spectra are apparently similar except for the absorption around 3400 cm^{-1} assignable to the O-H stretching. Consequently, it can be concluded that, concerning the conductivities, the influence of the environment on the $ZnCl_2$-EMIC melt is slight and this melt can be classified as stable.

Conclusions

The sequence of conductivities for the three binary melt systems is $ZnCl_2$-EMIC > $ZnCl_2$-BPC > $ZnCl_2$-BTEAC. In the $ZnCl_2$-BPC system, the conductivities at 70 to 150 °C have a maximum at 40 mol% $ZnCl_2$. The lowest activation energy is observed at 25.21 kJ/mol for the $ZnCl_2$-EMIC system; its conductivity is constant from 30 to 50 mol% $ZnCl_2$, while it considerably increases from 70 to 150 °C. As to the $ZnCl_2$-BTEAC system, the conductivities in the range 110 - 170 °C gradually decrease for 30 to 60 mol% $ZnCl_2$.

A comparison of the electrical conductivities of $ZnCl_2$-EMIC melts with those of the $AlCl_3$-EMIC melts previously studied indicates that the two melt systems have a similar tendency as to temperature, and that a temperature higher by about 40 °C is needed for the $ZnCl_2$-EMIC melt system to have comparable conductivities with those of $AlCl_3$-EMIC.

The stability of the $ZnCl_2$-EMIC system has also been examined, and it may be concluded that the effect of the environment is slight and that the $ZnCl_2$-EMIC melt can be classified as stable.

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[1] C. L. Hussey, Electrochem. **67**, 527 (1999).
[2] H. -Y. Hsu and C. -C. Yang, Z. Naturforsch. **56a**, 670 (2001).
[3] N. Koura, T. Endo, and Y. Idemoto, J. Non-Cryst. Sol. **205-207**, 650 (1996).
[4] Y.-F. Lin and I. -W. Sun, Electrochim. Acta **44**, 2771 (1999).
[5] P.-Y. Chen, M. -C. Lin, and I. -W. Sun, J. Electrochem. Soc. **147**, 3350 (2000).
[6] P.-Y. Chen and I.-W. Sun, Electrochim. Acta **46**, 1169 (2001).
[7] R. A. Carpio, L. A. King, F. C. Kibler, Jr., and A. A. Fannin, Jr., J. Electrochem. Soc. **126**, 1650 (1979).
[8] K. Ito, N. Nishina, and H. Ohno, Electrochim. Acta **45**, 1295 (2000).
[9] J. D. Edwards, C. S. Taylor, A. S. Russell, and L. F. Maranville, J. Electrochem. Soc. **90**, 527 (1952).
[10] H. Every, A. G. Bishop, M. Forsyth, and D. R. MacFarlane, Electrochim. Acta **45**, 1279(2000).
[11] M. Hirao, K. Ito, and H. Ohno, Electrochim. Acta **45**, 1291 (2000).
[12] D. R. McFarlane, J. Sun, J. Golding, P. Meakin, and M. Forsyth, Electrochim. Acta **45**, 1271 (2000).
[13] A. J. Easteal and C. A. Angell, J. Phys. Chem. **74**, 3987 (1970).
[14] C. A. Angell and D. M. Gruen, J. Phys. Chem. **70**, 1601 (1966).
[15] W. E. Smith, J. Brynestad, and G. P. Smith, J. Chem. Phys. **52**, 3890 (1970).
[16] S. J. Cyvin, P. Klaboe, E. Rytter, and H. A. Oye, J. Chem. Phys. **52**, 2776 (1970).
[17] Y. Castrillejo, M. A. Gracia, A.-M. Martinez, C. Abejon, P. Pasquer, and G. Picard, J. Electroanal. Chem. **434**, 43 (1997).
[18] R. B. Ellis, J. Electrochem Soc. **113**, 485 (1966).
[19] H. Hayashi, K. Uno, Z.-I. Takehara, and A. Katagiri, J. Electrochem. Soc. **140**, 386 (1993).