Korean J. Chem. Eng., **23**(5), 795-799 (2006)

Thermal and electrochemical properties of ionic liquids based on N-methyl-N-alkyl morpholinium cations

Sukjeong Choi, Ki-Sub Kim, Jong-Ho Cha, Huen Lee†, Jae Seung Oh* and Byoung-Bae Lee*

Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology,
373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Korea
*LG Chemical, Ltd., PO Box 61, Daejeon 305-380, Korea
(*Received 28 November 2005 • accepted 7 March 2006*)

Abstract−A series of ionic liquids based on morpholinium cations were prepared. N-alkyl-N-methylmorpholinium bromide, N-alkyl-N-methylmorpholinium tetrafluoroborate, N-alkyl-N-methylmorpholinium hexafluorophosphate and N-alkyl-N-methylmorpholinium bis(trifluoromethanesulfonyl)imide were synthesized, and then thermal and electrochemical properties of prepared ionic liquids were measured. These morpholinium salts were found to be thermally stable near 673 K and electrochemically stable up to 6 V at room temperature. In conclusion, these new series of morpholinium based ILs might be potential candidates for electrolytes in batteries and other electrolytic devices.

Key words: Ionic Liquids, Electrochemical Property, N-alkyl-N-methylmorpholinium Bromide ([Mor][Br]), N-alkyl-N-methylmorpholinium Tetrafluoroborate ([Mor][BF_4]), N-alkyl-N-methylmorpholinium Hexafluorophosphate ([Mor][PF_6]), and N-alkyl-N-methylmorpholinium Bis(trifluoromethanesulfonyl)imide ([Mor][TFSI]), Lithium Doped Electrolyte

INTRODUCTION

During the last decade, various mixtures of organic carbonates with cyclic and non-cyclic groups have been used in electrolytic systems because of their high electric conductivity [Ding et al., 2000]. However, these binary solvents tend to result in a low performance due to the narrow potential window and the lack of safety. In recent years, ionic liquids (ILs) have been used as electrolytes in electrolytic devices such as solar cells, capacitors and fuel cells [Sato et al., 2004; Souza et al., 2003]. The popularity of ILs is due to the following characteristics that are intrinsically suitable for electrolytes: (1) low vapor pressure, (2) negligible-flammability, (3) high thermal stability, (4) electrochemical stability, and (5) high ionic conductivity [Quinn et al., 2002; Hagiwara et al., 2002; Bradley et al., 2000]. ILs are expected to improve the stability and durability of electrolytic systems.

Generally, ILs have been synthesized by a combination of large heterocyclic organic cations, alkyl substituents and inorganic anions. The organic cations that have been widely used include quaternary ammonium [Sun et al., 1988], pyrrolidinium [MacFarlane et al., 1999], and imidazolium [Blanchard et al., 1999], though the synthesis of these cations is complex and costly. The commonly used inorganic anions are halides such as $[AlCl_4]^-$, $[BF_4]^-$, $[PF_6]^-$ and $[CF_3SO_2]^-$. By varying the cations, substituents, and anions, it becomes possible to produce target-specific changes in the chemical and physical properties of ILs [Huddleston et al., 1998; Kim et al., 2004a; Marsh et al., 2002]. For example, the water solubility of ILs in the same cation could be controlled by the unique characteristics of anion species. In the case of the imidazolium salts, 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) appears to be soluble in water, while 1-ethyl-3-methylimidazolium hexafluorophosphate ($EMIMPF_6$) is immiscible [Qin et al., 2003].

In most cases, we can easily synthesize ILs with designed structures, but we need careful and complicated purification processes to obtain pure ILs because the impurities are very difficult to remove completely. Accordingly, impurities in metathesis reactants also affect the characteristics of ILs such as the melting point, viscosity, and ionic conductivity. Specifically, in the present study we tried to evaluate the thermal electrochemical characteristics of synthesized ILs based on N-methyl morpholinium cation. Morpholinium salts might be applicable to electrolytes for several reasons. For instance, when ILs based on a morpholinium cation are used as the electrolytes for batteries, the oxygen group in the cation could dissociate the Li salts and the ionic conductivity might consequently be enhanced. In addition, ILs can be conveniently synthesized because of their good product reproducibility, easy purification process and short processing time. Moreover, methylmorpholine is less expensive than other organic cations such as pyrrolidinone and methylimidazole [Kim et al., 2004b].

Here, we report three series of N-methyl morpholinium salts with tetrafluoroborate, hexafluorophosphate and bis(trifluoromethanesulfonyl)imide having a high purity. Also, we investigate how the changes of the alkyl chain length have an impact upon their physical properties. Through careful examinations of their basic thermal and electrochemical characteristics, we will check the possibility for their wide applications in electrochemical fields.

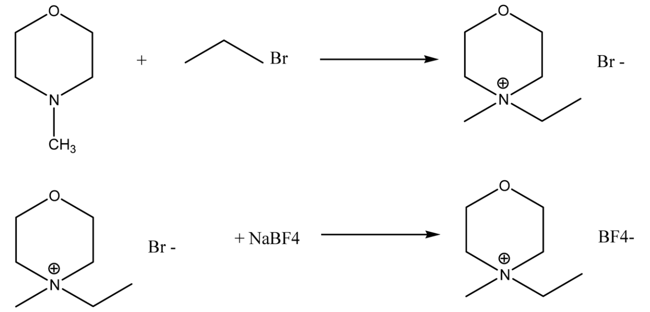
EXPERIMENTAL SECTION

1. Analysis

To record ^1H NMR mass spectra, we used a Bruker DMX 600 MHz NMR spectrometer, and to record FAB mass spectra, we used an FAB mass JMS-HX110A. The contents of residual Br-ions were

---

†To whom correspondence should be addressed.
E-mail: h_lee@kaist.ac.kr



Scheme 1. Synthesis process of morpholinium cation based IL.

detected with the aid of ion chromatography (System : Bio-LC DX-300 (Dionex, Sunny-vale, CA, USA), Detector : Suppressed Conductivity (PED2), Column : ICSep AN300 with ICSep ANSC guard). We also used the PA instrument TGA 2050 to determine the thermal stability of morpholinium salts under nitrogen gas at a heating rate of 10 K·min^{-1}. In addition, we used a Dupont TA 2000 differential scanning calorimeter to examine the temperature-dependent phase behavior in a temperature range of 123.15 K to 423.15 K under nitrogen gas at a heating rate of 10 K·min^{-1}. Finally, we used a cyclic voltammetry Solatron 1287A to measure the electrochemical stability. We obtained the value of electrochemical stability with a scan rate of 20 mV·s^{-1} and used a 3 mm diameter glassy carbon as a working electrode and also used a platinum wire as a counter electrode and a silver wire as a reference electrode.

2. Synthesis of Ionic Liquids

We prepared N-alkyl-N-methyl morpholinium Bromide [Mor][Br], N-alkyl-N-methyl morpholinium Tetrafluoroborate [Mor][BF$_4$], N-alkyl-N-methyl morpholinium hexafluorophosphate [Mor][PF$_6$] and N-alkyl-N-methyl morpholinium bis(trifluoromethanesulfonyl)imide [Mor][TFSI] with a method from the literature [Kim et al., 2004b; Choi et al., 2005]. We obtained N-methylmorpholine, bromoethane, butyl-bromide, octyl-bromide, potassium hexafluorophosphate (KPF$_6$), and sodium borofluoride (NaBF$_4$) from Aldrich, and received acetonitril and dichloroethane from MERCK. All the materials used in the experiments were used without additional further treatment. The N-alkyl-N-methyl morpholinium cation with the linear alkyl substituents was prepared by in a two-step reaction using acetonitrile. After ion exchanging, they were purified by the following methods. After filtering by the filter paper, they were repeatedly washed with a mixture of water and dichloromethane for removing the by-product. The final products were dried under vacuum at 313.15 K for more than 48 h and kept under N$_2$ gases. To analyze the purity of the ILs, we used ^{1}H-NMR and Fab Mass spectra. We also recorded the halide content, which is important because the physical and electrochemical properties depend on the content of halogen anions.

2-1. N-ethyl-N-methyl Morpholinium Bromide [Mor$_{1,2}$][Br]

^{1}H-NMR (DMSO, δ/ppm, relative to TMS) 3.92-3.90 (4H), 3.56-3.49 (2H), 3.42-3.39 (4H), 3.11 (3H), 1.28-1.23 (3H). FAB MS : m/z=130 [Mor$_{1,2}$]$^+$.

2-2. N-ethyl-N-methyl Morpholinium Tetrafluoroborate [Mor$_{1,2}$][BF$_4$]

^{1}H-NMR (Acetone, δ/ppm, relative to TMS) 4.14-4.04 (4H), 3.79-3.75 (2H), 3.67-3.61 (4H), 3.39-3.36 (3H), 1.50-1.46 (3H). FAB MS : m/z=130 [Mor$_{1,2}$]$^+$. Br-content : 5.6 ppm.

2-3. N-ethyl-N-methyl Morpholinium Hexafluorophosphate [Mor$_{1,2}$][PF$_6$]

^{1}H-NMR (Acetone, δ/ppm, relative to TMS) 4.16-4.07 (4H), 3.82-3.78 (2H), 3.69-3.66 (4H), 3.40 (3H), 1.52-1.48 (3H). FAB MS : m/z=130 [Mor$_{1,2}$]$^+$. Br- content : 57.4 ppm.

2-4. N-ethyl-N-methyl Morpholinium Bis(trifluoromethanesulfonyl)imide [Mor$_{1,2}$][TFSI]

^{1}H-NMR (D$_2$O, δ/ppm), 4.08 (m, 4H), 3.59-3.50 (m, 6H), 3.19 (s, 3H), 1.41 (t, 3H). FAB MS : m/z=130.00 [Mor$_{1,2}$]$^+$. Br-content : not detected by ion chromatography.

2-5. N-butyl-N-methyl Morpholinium Bromide [Mor$_{1,4}$][Br]

^{1}H-NMR (DMSO, δ/ppm, relative to TMS) 3.92-3.9 (4H), 3.50-3.39 (6H), 3.16 (3H), 1.72-1.62 (2H), 1.39-1.36 (2H), 0.96-0.91 (3H). FAB MS : m/z=158 [Mor$_{1,4}$]$^+$.

2-6. N-butyl-N-methyl Morpholinium Tetrafluoroborate [Mor$_{1,4}$][BF$_4$]

^{1}H-NMR (Acetone, δ/ppm, relative to TMS) 4.12-4.03 (4H), 3.67-3.60 (6H), 3.36 (3H), 1.92-1.85 (2H), 1.48-1.40 (2H), 1.00-0.97 (3H). FAB MS : m/z=158 [Mor$_{1,4}$]$^+$. Br-content : 145 ppm.

2-7. N-butyl-N-methyl Morpholinium Hexafluorophosphate [Mor$_{1,4}$][PF$_6$]

^{1}H-NMR (Acetone, δ/ppm, relative to TMS) 4.13-4.11 (4H), 3.73-3.67 (6H), 3.43 (3H), 1.96-1.90 (2H), 1.48-1.43 (2H), 1.01-0.98 (3H). FAB MS : m/z=158 [Mor$_{1,4}$]$^+$. Br-content : 80.1 ppm.

2-8. N-butyl-N-methyl Morpholinium Bis(trifluoromethanesulfonyl)imide [Mor$_{1,4}$][Br]

^{1}H-NMR (D$_2$O, δ/ppm), 4.08 (m, 4H), 3.56-3.47 (m, 6H), 3.21 (s, 3H), 1.82-1.80 (m, 2H), 1.46-1.42 (m, 2H), 1.01-0.98 (t, 3H). FAB MS : m/z=158 [Mor$_{1,4}$]$^+$. Br-content : not detected by ion chromatography.

2-9. N-octyl-N-Methyl morpholinium Bromide [Mor$_{1,8}$][Br]

^{1}H-NMR (DMSO, δ/ppm, relative to TMS) 3.92-3.90 (4H), 3.49-3.41 (6H), 3.15 (3H), 1.69-1.65 (2H), 1.3 (4H), 1.28 (6H), 0.89 (3H). FAB MS : m/z=214 [Mor$_{1,8}$]$^+$.

2-10. N-octyl-N-methyl Morpholinium Tetrafluoroborate [Mor$_{1,8}$][BF$_4$]

^{1}H-NMR (Acetone, δ/ppm, relative to TMS) 4.13-4.05 (4H), 3.70-3.63 (6H), 3.39 (3H), 1.97-1.90 (2H), 1.44-1.36 (4H), 1.35-1.26 (6H), 0.88-0.86 (3H). FAB MS : m/z=214 [Mor$_{1,8}$]$^+$. Br- content : 101.1 ppm.

2-11. N-octyl-N-methyl Morpholinium Hexafluorophosphate [Mor$_{1,8}$][PF$_6$]

^{1}H-NMR (Acetone, δ/ppm, relative to TMS) 4.12-4.11 (4H), 3.73-3.66 (6H), 3.44 (3H), 1.98-1.95 (2H), 1.45-1.38 (4H), 1.35-1.26 (6H), 0.88-0.86 (3H). FAB MS : m/z=214 [Mor$_{1,8}$]$^+$. Br-content : 89.3 ppm.

RESULTS AND DISCUSSION

1. Thermal Properties

All of the morpholinium salts were measured with differential scanning calorimeter. Thermal properties of ionic liquids were summarized in Table 1. Fig. 1 shows the differential scanning calorimetry traces for the [BF$_4$]$^-$ anion series, while Fig. 2 illustrates those of the [PF$_6$]$^-$ anion series. Higher thermal stability was provided by the following sequence, such as [Mor][PF$_6$]>[Mor][BF$_4$]>[Mor][TFSI]. Although [BF$_4$]$^-$ is smaller than [PF$_6$]$^-$, [Mor][BF$_4$] has a lower melting temperature than [Mor][PF$_6$]. The lower melting points might suggest a small ion radius. However, it is also known that the melt-

Table 1. Summary of ionic liquids

	Ionic liquids							
	$[Mor_{1,2}]$ $[BF_4]$	$[Mor_{1,4}]$ $[BF_4]$	$[Mor_{1,8}]$ $[BF_4]$	$[Mor_{1,2}]$ $[PF_6]$	$[Mor_{1,4}]$ $[PF_6]$	$[Mor_{1,8}]$ $[PF_6]$	$[Mor_{1,2}]$ [TFSI]	$[Mor_{1,4}]$ [TFSI]
Melting temperature (K)	85.53	78.28	50.51	86.70	94.86	107.83	29.2	28.7
Decomposition temperature (K)	653.15	673.15	523.15	653.15	653.15	623.15	673.15	673.15
Electrochemical stability (V)			6.39	6.14	6.11	6.25	4.5	4.5

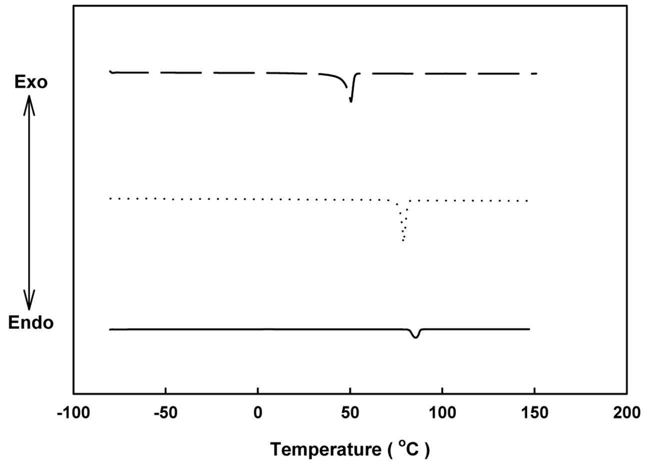


Fig. 1. DSC trace of $[Mor_{1,2}][BF_4]$ (– –), $[Mor_{1,4}][BF_4]$ (·······), $[Mor_{1,8}]$ $[BF_4]$ (——).

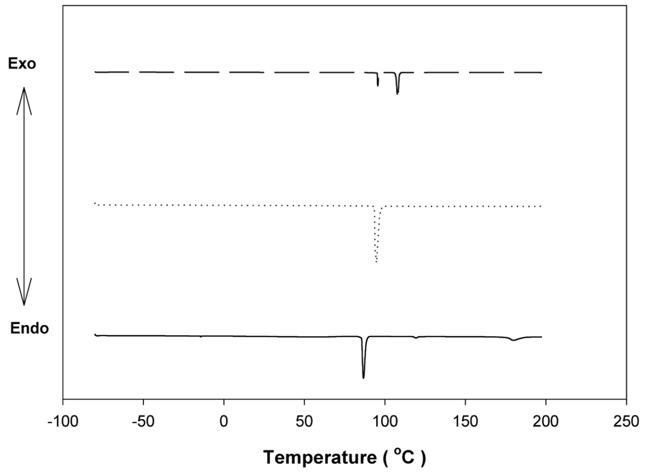


Fig. 2. DSC trace of $[Mor_{1,2}][PF_6]$ (– –), $[Mor_{1,4}][PF_6]$ (·······), $[Mor_{1,8}]$ $[PF_6]$ (——).

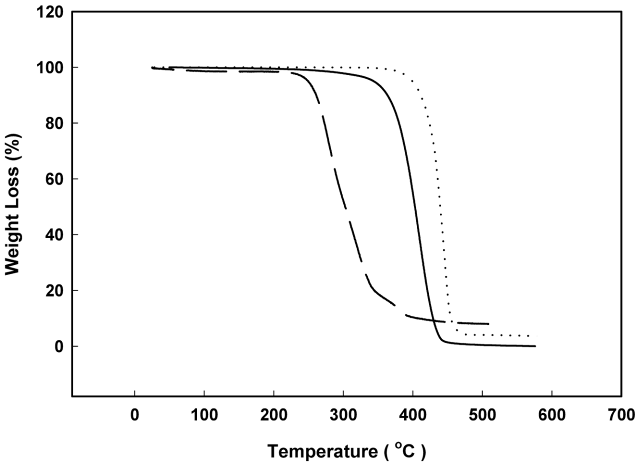


Fig. 3. Thermal gravimetric analysis of $[Mor_{1,2}][BF_4]$ (– –), $[Mor_{1,4}]$ $[BF_4]$ (·······), $[Mor_{1,8}][BF_4]$ (——).

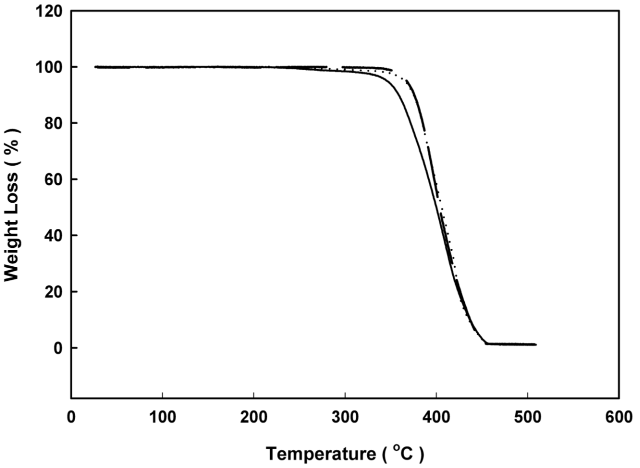


Fig. 4. Thermal gravimetric analysis of $[Mor_{1,2}][PF_6]$ (– –), $[Mor_{1,4}]$ $[PF_6]$ (·······), $[Mor_{1,8}][PF_6]$ (——)

ing temperature might be affected by other factors such as the physico-chemical characteristics [Ohno et al., 2002]. In our experiments, $[Mor][BF_4]$ and $[Mor][PF_6]$ showed a different tendency. The melting point of $[Mor][BF_4]$ falls with increasing alkyl chain length; however, those of $[Mor][PF_6]$ increase with increasing alkyl chain length. In this case, anion species might affect the melting point. There should be a close relation between ion packing and structure. The melting point of the $[TFSI]^-$ salts is much lower than the melting points of $[BF_4]^-$ and $[PF_6]^-$, and the melting point of [Mor] [TFSI] is near room temperature [Kim et al., 2004b]. To depress the melting temperature, the $[TFSI]^-$ salts were generally used as the anion sources of ILs [Bonhote et al., 1996; McEwen et al., 1999]. In tetraalkylammonium or N,N-dialkyl-pyrrolidinium salts, the $[TFSI]^-$ anions significantly decrease the melting point corresponding to the halides [Forsyth et al., 2002]. Fig. 2 illustrates the thermal properties of a series of N-alkyl-N-methylmorpholinium salts with $[PF_6]^-$ anion. There is two-phase transition in $[Mor_{1,8}][PF_6]$, 1-2 phase transition occurs at 368.76 K and a 2-3 phase transition occurs at 380.98 K. Some properties of $[Mor_{1,8}][PF_6]$ might change around the transition temperature.

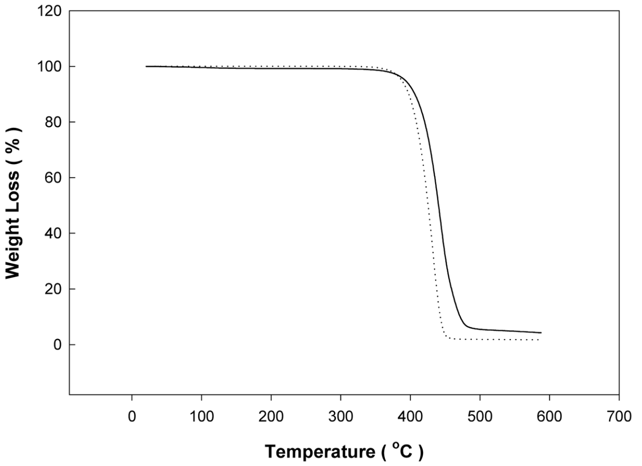


Fig. 5. Thermal gravimetric analysis of [Mor$_{1,2}$][TFSI] (– –), [Mor$_{1,4}$][TFSI] (·······).

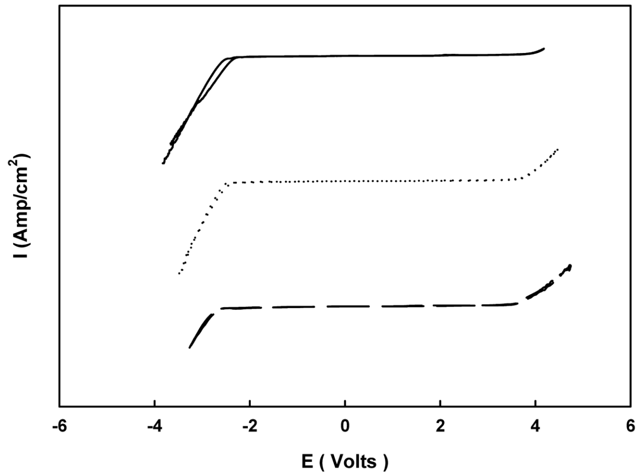


Fig. 6. Cyclic voltammograms of [Mor$_{1,2}$][PF$_6$] (– –), [Mor$_{1,4}$][PF$_6$] (·······), [Mor$_{1,8}$][PF$_6$] (——).

Fig. 3, Fig. 4 and Fig. 5 show the thermogravimetric analysis traces of morpholinium cationed materials, though the thermal data of [Mor$_{1,2}$] [TFSI] were taken from our previous study [Kim et al., 2004b]. In their three figures, we can see various side alkyl chains including ethyl, butyl, and octyl, and most of the morpholinium salts decomposed near 673 K except [Mor$_{1,8}$][BF$_4$]. As with common ILs, these materials have proven to be stable until the temperature nears 673 K. In the second reaction, [Mor$_{1,2}$][Br] is used as a source material for all the products, namely [Mor$_{1,2}$][BF$_4$], [Mor$_{1,2}$][PF$_6$], and [Mor$_{1,2}$][TFSI]. By changing the anion species in the second reaction, there is a surprising improvement in the decomposition temperature of [Mor$_{1,2}$][BF$_4$], [Mor$_{1,2}$][PF$_6$] and [Mor$_{1,2}$][TFSI]. The highest thermal stability is found in [Mor$_{1,2}$][TFSI], though, [Mor$_{1,2}$] [BF$_4$] and [Mor$_{1,2}$][PF$_6$] were also thermally stable until the temperature nears 673 K. All of the prepared ILs besides [Mor$_{1,8}$][PF$_6$] have a melting point below 373 K to make them candidates for ionic liquid. Particularly, [Mor$_{1,2}$][TFSI] and [Mor$_{1,4}$][TFSI] opens the possibility to potential application, because their melting points are sufficiently low and their decomposition temperatures are very high.

2. Electrochemical Properties

To analyze the behavior of each series, we used a cyclic voltammetry Solatron 1287A potentiostat/galvanostat at room temperature, and we obtained the value of electrochemical stability with a scan rate of 20 mV·s^{-1}. For the electrochemical cell, we used a 3 mm diameter glassy carbon as a working electrode; we also used a platinum wire as a counter electrode and a silver wire as a reference electrode. Fig. 6 shows that of the [PF$_6$]$^-$ anion series. The absolute value of the potential windows was 6.39 V for [Mo$_{1,8}$][BF$_4$]; and the potential windows were 6.14 V for [Mor$_{1,2}$][PF$_6$], 6.11 V for [Mor$_{1,4}$] [PF$_6$], and 6.25 V for [Mor$_{1,8}$][PF$_6$]. The values of electrochemical window of prepared ionic liquids are also described in Table 1. These morpholinium salts are electro-stable up to 6 V versus Ag/Ag+ at room temperature. An irreversible reduction potential occurred around −2.2 V to −2.3 V versus Ag/Ag+, and irreversible oxidation occurred around +4.0 V versus Ag/Ag+. The [Mor][BF$_4$] and [Mor][PF$_6$] salts have similar cathodic limits to [Mor][TFSI], but their anodic limits are higher than the [Mor][TFSI] [Kim et al., 2004b]. These results of the morpholinium salts suggest that both [Mor][BF$_4$] and [Mor][PF$_6$] show remarkable electrochemical stability above 6 V, and that the [BF$_4$]$^-$ series is more stable than the [PF$_6$]$^-$ series. In addition, [Mor][BF$_4$] and [Mor][PF$_6$] have larger electrochemical windows than [Mor][TFSI], [Mor][TFSI] has electrochemical stability about 4 V.

The results also indicate that these salts could have practical application in items such as batteries and capacitors. Furthermore, in an overall comparison of [Mor][TFSI] and [IM(imidazolium)][TFSI], the morpholinium and salts have lower conductivities than the imidazolium salts [McEwen et al., 1999]. The imidazolum salts are the most widely studied because they have good characteristics such as low viscosity and high ionic conductivity [Hagiwara et al., 2000; Ngo et al., 2000]. However, the possible reactions of C2 carbon in 1-alkyl and 3-alkyl imidazolium might raise questions about their electrochemical stability [MacFarlane et al., 1999]. Therefore, compared with imidazolium salts, the morpholinium salts have lower ionic conductivity due to the higher melting point, but they have the strength of high electrochemical stability such as wider electrochemical windows than conventional ionic liquid based on imidazolium cation.

CONCLUSION

Using two-step reactions, we prepared a new series of morpholinium salts with tetrafluoroborate, hexafluorophosphate and bis(trifluoromethanesulfonyl)imide anions. We report their synthetic procedures and physical and electrochemical properties. All the synthesized ILs were found to be in a solid state at room temperature. When compared to common ILs such as imidazolium and pyrrolidinium salts, the materials that we synthesized possessed two process merits such as a short synthetic time and simple purification step. Moreover, it might be worthwhile to note that morpholinium cations are far cheaper than other cation sources. Most of them decompose near 673 K with high electrochemical windows up to 4 V, and [Mor][BF$_4$] and [Mor][PF$_6$] in particular show that new ILs are electrochemically stable over 6 V.

ACKNOWLEDGMENT

This work was supported by the Brain Korea 21 Project and also partially funded by LG Chemical. We would like to thank KBSI (Korea Basic Science Institute) for assistance with NMR, FAB mass and ion chromatography.

REFERENCES

Blanchard, L. A., Hancu, D., Beckman, E. J. and Brennecke, J. F., "Green processing using ionic liquids and Co_2," *Nature*, **99**, 28 (1999).

Bonhote, P., Dias, A.-P., Armand, M., Papageorgiou, N., Kalyanasundaram, K. and Gratzel, M., "Hydrophobic, highly conductive ambient-temperature molten salts," *Inorg. Chem.*, **35**, 1168 (1996).

Bradley, D., Dyson, P. and Welton, T., "An ion brew for cleaner chemistry," *Chem. Rev.*, **9**(5), 18 (2000).

Choi, S., Kim, K.-S., Lee, H., Oh, J. S. and Lee, B.-B., "Synthesis and ionic conductivities of lithium doped morpholinium salts," *Korean J. Chem. Eng.*, **22**, 281 (2005).

de Souza, R. F., Padilha, J. C., Gonçalves, R. S. and Dupont, J., "Room temperature dialkylimidazolium ionic liquid-based fuel cells," *Electrochem. Commun.*, **5**, 728 (2003).

Ding, M. S., Xu, K. and Jow, T. R., "Liquid-solid phase diagrams of binary carbonates for lithium batteries," *J. Electrochem. Soc.*, **147**, 1688 (2000).

Forsyth, C. M., MacFarlane, D. R., Golding, J. J., Huang, J., Sun, J. and Forsyth, M., "Structural characterization of novel ionic materials incorporating the bis(trifluoromethanesulfonyl)amide anion," *Chem. Mater.*, **14**, 2103 (2002).

Hagiwara, R. and Ito, Y., "Room temperature ionic liquids of alkylimidazolium cations and fluoroanions," *J. Fluorine Chem.*, **105**, 221 (2000).

Hagiwara, R. and Ito, Y., "Room temperature molten fluorometallates: 1-ethyl-3-methylimidazolium hexafluoroniobate (V) and hexafluorotantalate (V)," *J. Fluorine Chem.*, **221**, 133 (2002).

Huddleston, J. G., Willauer, H. D., Swatloski, R. P., Visser, A. E. and Rogers, R. D., *Chem. Commun.*, 1765 (1998).

Kim, K. S., Choi, S., Demberelnyamba, D., Lee, H., Oh, J., Lee, B. B. and Mun, S. J., "Ionic liquids based on *N*-alkyl-*N*-methylmorpholinium salts as potential electrolytes," *Chem. Commun.*, 828 (2004b).

Kim, K.-S., Shin, B.-K. and Lee, H., "Physical and electrochemical properties of 1-butyl-3-methylimidazolium bromide, 1-butyl-3-methylimidazolium iodide, and 1-butyl-3-methylimidazolium tetrafluoroborate," *Korean J. Chem. Eng.*, **21**, 1010 (2004a).

MacFarlane, D. R., Meakin, P., Sun, J., Amini, N. and Forsyth, M., "Pyrrolidinium imides: A new family of molten salts and conductive plastic crystal phases," *J. Phys. Chem. B*, **103**, 4164 (1999).

Marsh, K. N., Deev, A., Wu, A. C.-T., Tran, E. and Klamt, A., "Room temperature ionic liquids as replacements for conventional solvents - A review," *Korean J. Chem. Eng.*, **19**, 357 (2002).

McEwen, A. B., Ngo, H. L., LeCompte, K. and Goldman, J. L., "Electrochemical properties of imidazolium salt electrolytes for electrochemical capacitor applications," *J. Electrochem. Soc.*, **146**, 1687 (1999).

Ngo, H. L., Lecompte, K., Hargens, L. and McEwen, A. B., "Thermal properties of imidazolium ionic liquids," *Thermochimica Acta.*, **97**, 357 (2000).

Ohno, H. and Yoshizawa, M., "Ion conductive characteristics of ionic liquids prepared by neutralization of alkylimidazoles," *Solid State Ionics*, **154/155**, 303 (2002).

Qin, W., Wei, H. and Li, S. F. Y., "1,3-Dialkylimidazolium-based room-temperature ionic liquids as background electrolyte and coating material in aqueous capillary electrophoresis," *J. Chromatogr. A*, **985**, 447 (2003).

Quinn, B. M., Ding, Z., Moulton, R. and Bard, A. J., "Novel electrochemical studies of ionic liquids," *Langmuir*, **18**, 1734 (2002).

Sato, T., Masuda, G. and Takagi, K., "Electrochemical properties of novel ionic liquids for electric double layer capacitor applications," *Electrochim. Acta*, **49**, 3603 (2004).

Sun, J., Forsyth, M. and MacFarlane, D. R., "Room-temperature molten salts based on the quaternary ammonium ion," *J. Phys. Chem. B*, **102**, 8858 (1988).