The Preparation of Nonaqueous Electrolytes Based on Quaternary Imidazolium Salts for EDLC

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Quaternary salts were prepared and characterized to use in an electrolyte for EDLC. Salts consisting of cation (1-methyl-3-ethyl imidazolium, 1,2-diethyl-3-methyl imidazolium, or tetraethyammonium) and anion (hexafluorophosphate, tetrafluoroborate, or perchlorate) had been synthesized. Qauternarization reaction performed by using ethyl bromide as a quaternary agent. Unlike other halide agents, reaction was progressed in liquid phase at room temperature with high efficiency (above 90%). Hexafluorophosphate, tetrafluoroborate, or perchlorate was exchanged with bromide through double decomposition. For synthesized salts, purity was verified by IC and ICP, and structures were confirmed by ^{1}H-NMR, ^{19}F-NMR, and IR. Imidazolium salts had higher exothermic degradation temperature (350~400℃) than ammonium salts (250~300℃). Thermal stability was improved in order of PF_6^- >BF_4^- >ClO_4^- for anions and 1, 2-dimethyl-3-ethylimidazolium >1-methyl-3-ethylimidazolium >tetraethyammonium for cations. Ionic conductivities of electrolytes containing 1M of imidazolium salts in propylene carbonate (14.12 mS/cm at 25^{o}C) were much higher than that of electrolytes containing 1M of ammonium salts (11.29 mS/cm at 25^{o}C). Also, the electrolyte containing PF_6^- or $BF`_4^-$ was more conductive than the electrolyte containing ClO_4^-. Such trends were confirmed with AC impedance analysis. Maximum solubilities of ammonium and imidazolium salts at room temperature were 1M and 1.6M in propylene carbonate. From cyclic voltammogram, the stability window of electrolyte based on imidazolium salts had about 2 V larger than that of electrolyte based on quaternary ammonium salts. As conclusion, the 1.6M of 1-methyl, 3-ethylimidazolium hexafluorophosphate in propylene carbonate was superior to others in the thermal stability, ionic conductivity, and electrochemical stability windows. Rating characteristics of EDLC with imidazolium based electrolytes should be investigated in near future.

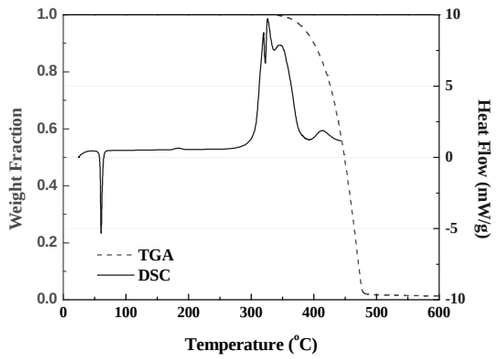

Fig. 1. Thermal analysis of 1-methyl-3-ethylimidazolium hexafluorophosphate

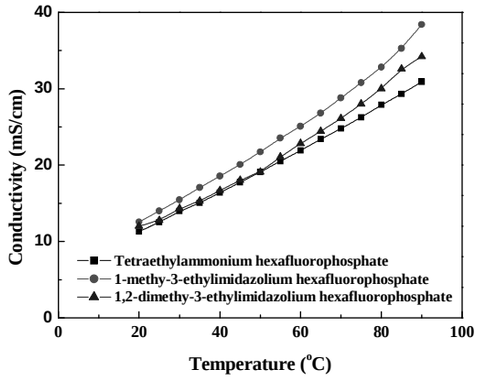

Fig. 2. Temperature dependences of ionic conductivity of 1M electrolyte in propylene carbonate

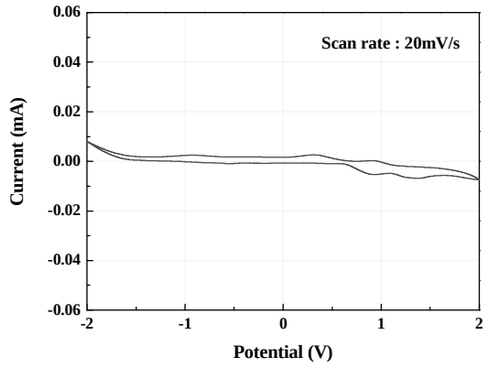

Fig. 3. The cyclic voltammogram of 1-methyl-3-ethylimidazolium hexafluorophosphate (1M in propylene carbonate)