



# Allyl-functionalized ionic liquids as electrolytes for electric double-layer capacitors

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## ABSTRACT

Double-layer capacitor electrolytes employing allyl-functionalized ionic liquids as electrolytes with solvents have been evaluated. Imidazolium cations with allyl groups enabled the high capacitances and low resistances of electric double-layer capacitor (EDLC) cells at a wide range of temperature in spite of the large cation sizes and low ionic conductivities of the electrolytes compared to imidazolium with saturated alkyl groups, 1-ethyl-3-methylimidazolium (EMIm). The improvement of EDLC performance was noted particularly in the case of diallylimidazolium (DAIm) cation and TFSAnion. The substitution of the vinyl group increased the high capacitance only at 298 K and decreased the capacitance at low temperature and direct current resistance (DC-IR) at 243 and 298 K. The butenyl group deteriorated the capacitance and DC-IR at 243 and 298 K. The stability of EDLC cell of DAIm-BF<sub>4</sub>/PC was inferior to that of EMIm-BF<sub>4</sub>/PC. The addition of DMC to PC improved the stability.

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## 1. Introduction

Ionic liquids (ILs) have received a lot of interest recently as the ion conductive materials as well as the reaction media because of the unusual properties of ILs such as a wide liquid range, high ionic conductivities, a wide voltage window, non-volatility, and non-flammability [1–5]. In addition, the designability of ILs makes themselves attractive alternatives to the conventional organic electrolytes and solvent systems. The common ILs are imidazolium and pyridinium derivatives [6,7]. Phosphonium and tetraalkylammonium compounds can be also used for the same purpose [8,9].

Recently some studies have been reported to improve the high-temperature safety and durability of electrochemical devices such as lithium rechargeable batteries [10], electric double-layer capacitors (EDLCs) [11–15], and titanium oxide dye-sensitized solar cells [16].

For EDLC electrolytes, various solvents and salts are available, offering specific advantages such as a high capacitance and low temperature performances. Generally, the organic electrolyte, which is the solid quaternary ammonium salt dissolved in the high dielectric constant solvent, has been used for high voltage EDLCs of 2 or higher than 2 V. Here, the salt is *N,N,N,N*-tetraethylammonium-BF<sub>4</sub> (TEA-BF<sub>4</sub>) or *N,N,N*-triethyl-

methyammonium-BF<sub>4</sub> (TEMA-BF<sub>4</sub>) and the solvent is propylene carbonate (PC). EDLCs store electricity physically, not chemically, in contrast with the rechargeable batteries [17].

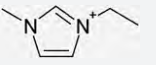
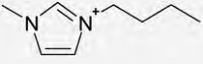
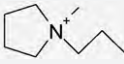
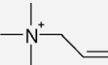
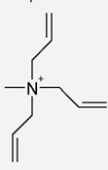
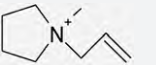
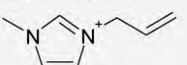
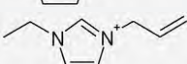
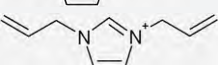
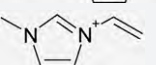
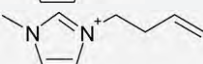
EDLCs have attracted much attention recently because of the power delivery performance that perfectly fills the gap between dielectric capacitors and traditional batteries. Recently, various salts for EDLCs such as salts of asymmetric ammonium, pyrrolidinium and piperidinium have been reported [18–20]. In addition, imidazolium-type ILs, such as 1-ethyl-3-methylimidazolium (EMIm), have been intensely researched because of the low viscosities, high ionic conductivities and low melting points.

Various ionic liquids of imidazolium cations having alkene or allyl groups were synthesized and the properties and the strong supercooling nature were reported [21–26]. However, the previously reported application was limited to the solvent for cellulose [27–29], the synthetic solvents [30], the electrolytes for the dye-sensitized solar cell [31], and the additive for lithium secondary batteries [32]. There has been no study on the application as salts for EDLC electrolytes of ILs with allyl groups.

Of special interest is to evaluate the performance of EDLC cells of ionic liquids and ammonium salts with saturated alkyl groups or olefinic substituents, including allyl, vinyl, and butenyl groups. In this paper we report on the ionic conductivities, the dynamic viscosities of EDLC electrolytes containing cations with allyl groups, the initial performances and the life tests of cells at a wide range of temperature. We also report on the effect of combined anions and solvents.

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**Table 1**  
Fundamental properties of the salts of various cations having allyl groups and TFSA anion at 298 K.

Code of salts	Structure of a cation	Viscosity/mPa s	Ionic conductivity/mS cm <sup>-1</sup>
EMIm-TFSA		31	8.9
BMIm-TFSA		52	3.9
Py13-TFSA		63	3.6
ATMA-TFSA		–	–
MTAA-TFSA		–	–
AMPy-TFSA		52	3.7
AMIm-TFSA		32	6.7
AEIm-TFSA		26	7.4
DAIm-TFSA		28	4.9
MVIm-TFSA		67	5.0
BTMIm-TFSA		44	3.9

## 2. Experimental

### 2.1. Preparation of various salts

The structures of salts studied in this study are shown in Table 1. The preparation of salts was carried out according to the standard procedures [21,22]. For example, we synthesized the 1-allyl-3-methylimidazolium (AMIm)-TFSA by the alkylation of 1-allylimidazole with iodomethane in acetonitrile, followed by the exchange reaction with LiTFSA in water. The high-grade salt of AMIm-TFSA was obtained after washing with excess purified water repeatedly for cleaning up, followed by the evacuation at 433 K for 3 h for dehydration. *N*-Allyl-*N,N*-dimethylamine, *N,N,N*-triallylamine, 1-methylpyrrolidine, vinylimidazole and methylimidazole were used as starting materials for the syntheses of allyltrimethylammonium (ATMA)-TFSA, methyltriallylammonium (MTAA)-TFSA, *N*-allyl-*N*-methylpyrrolidinium (AMPy)-TFSA, *N*-methyl-*N*-vinylimidazolium (MVIm)-TFSA and *N*-(1-butenyl)-*N*-methylimidazolium (BTMIm)-TFSA, respectively. The structures of the synthesized salts were confirmed by <sup>1</sup>H NMR (AV400M, Bruker Biospin) and the purities of these salts were measured by the ion chromatography (DX-100 and DX-120, DIONEX Co., Ltd.).

AMIm-TFSA: <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ/ppm relative to TMS): 9.09 (s, 3H), 7.71–7.69 (m, 2H), 6.09–5.99 (m, 1H), 5.38–5.27 (m, 2H), 4.84–4.83 (d, 2H), 3.86 (s, 3H).

ATMA-TFSA: 6.10–6.00 (m, 1H), 5.64–5.57 (t, 2H), 3.95–3.93 (d, 2H), 3.02 (s, 9H).

MTAA-TFSA: 6.12–6.02 (m, 1H), 5.67–5.63 (t, 2H), 3.92–3.87 (t, 2H), 2.90 (s, 1H); MVIm-TFSA: 9.39 (s, 1H), 8.12–8.11 (t, 1H),

7.79–7.78 (t, 1H), 7.31–7.25 (m, 1H), 5.94–5.38 (m, 1H), 3.89 (s, 3H).

BTMIm-TFSA: 9.08 (s, 1H), 7.74–7.67 (m, 2H), 5.81–5.71 (m, 1H), 5.08–5.03 (m, 2H), 4.27–4.24 (t, 2H), 3.85 (s, 3H), 2.59–2.50 (m, 2H).

AMPy-TFSA: 6.11–6.01 (m, 1H), 5.64–5.59 (m, 2H), 3.98–3.96 (d, 2H), 3.50–3.39 (m, 4H), 2.97 (s, 3H), 2.10 (s, 4H).

DAIm-TFSA, AEIm-TFSA, AMIm-BF<sub>4</sub>, and DAIm-BF<sub>4</sub> were purchased from Kanto Chemical Co., Ltd. As reference samples, EMIm-TFSA, BMIm-TFSA, *N*-methyl-*N*-propylpyrrolidinium (Py13)-TFSA, EMIm-BF<sub>4</sub>, and *N,N,N*-trimethyl *N*-propylammonium (TMPA)-TFSA were also purchased from Kanto Chemical Co., Ltd.

### 2.2. Preparation of electrolytes

The electrolytes were prepared by dissolving the salts in propylene carbonate (PC), dimethylcarbonate (DMC), or  $\gamma$ -butyrolactone (GBL). All the electrolytes were prepared in a glove box of Ar atmosphere. We used 1.4 M EMIm-BF<sub>4</sub>/PC, EMIm-TFSA/PC, and TEMA-BF<sub>4</sub>/PC as typical electrolytes. EMIm-TFSA and EMIm-BF<sub>4</sub> were purchased from Kanto Chemical Co., Ltd. 1.4 M TEMA-BF<sub>4</sub>/PC was purchased from Tomiyama Pure Chemical Industries, Ltd.

### 2.3. Characterization of salts and electrolytes

The viscosities and ionic conductivities of ionic liquid and electrolyte were measured by using viscometer (Tokyo Keiki Inc.), and conductivity meter (CM-201, DKK-TOA Co., Ltd.) with a pair of Pt-black electrodes, respectively. The purities of ionic liquid and salts were measured by using ion chromatograph (DX-100 and DX-120, Dionex Co., Ltd.). The amounts of water in electrolytes were measured by using Karl Fischer titration meter (MKC-610-NT, Kyoto Electronics Manufacturing, Co., Ltd.).

### 2.4. Measurements of EDLC performance

Two types of activated carbons whose average particle sizes are large or small were individually prepared by the carbonization of phenolic resin, followed by KOH-activation and the pulverization. The BET specific surface area and the average pore diameter were calculated from the nitrogen adsorption isotherm at 77 K using Surface Area Analyzer (AUTOSORB-1, Quantachrome Instruments) and the particle size distribution was measured by Laser Diffraction Particle Size Analyzer (SALD-3000J, Shimadzu Co., Ltd.). In order to prepare the electrode with active layer, we first mixed the ink suspension of activated carbon, acetylene black, and acrylic binder solution of *N*-methyl-2-pyrrolidone. We then spread the mixture with blade onto the aluminum foil of 20  $\mu$ m thick, dried at 353 K for 3 h in air and evacuated it for further drying at 353 K for 3 h. The electrode thus obtained, had the activated layer of 50  $\mu$ m thick whose composition is 85 wt% of activated carbon, 9 wt% carbon black, 3 wt% of CMC, and 3 wt% of PTFE, and was cut into circles of 15 mm diameter.

The coin-type capacitor cells were assembled in a glove box of Ar atmosphere. The cell was constructed by setting a couple of electrodes face to face, with a paper separator (Nippon Kodoshi Co., Ltd.) inserted between them. The concentrations of EMIm-TFSA, EMIm-BF<sub>4</sub>, and TEMA-BF<sub>4</sub>/PC solutions were 1.4 M.

The assembled cell was charged in a constant current (CC) mode from  $V=0-2.0$  V at a constant current  $I=320$  mA g<sup>-1</sup>, and then charged further to keep a constant voltage (2.0 V) for 2 h. It was then discharged to 0 V at a given temperature, 243–298 K, in a CC mode at a current  $I=320$  mA g<sup>-1</sup>. To carry out the EDLC testing, we used a TOSCAT charge-discharging system, from Toyo System Co., Ltd.

**Table 2**  
Fundamental properties of the salts of various cations having allyl groups and BF<sub>4</sub> anion at 298 K.

Code of salts	Structure of a cation	Viscosity/mPa s	Ionic conductivity/mS cm <sup>-1</sup>
TEMA-BF <sub>4</sub>		–	–
EMIm-BF <sub>4</sub>		32	13.6
AMIm-BF <sub>4</sub>		44	8.6
DAIm-BF <sub>4</sub>		50	6.2

The capacitance  $C$  was calculated from the relation  $C = It/V$ , where  $t$  indicates discharging time [29]. Capacitance was normalized by the mass of electrode active layer including the carbon black, CMC, and PTFE. The direct current resistance (DC-IR) was calculated from the IR drop on the discharge curve at various temperatures.

The thermal stability (=life test) of EDLC was performed by continuous charging at 2.5 V at 333 K, and the cell deterioration was monitored by measuring the capacitances and DC-IRs at 2.0 V at 243–298 K. All data was the average value of two cells.

### 3. Results and discussion

#### 3.1. Physicochemical properties of salts

At first we evaluated TFSA-based electrolytes, because we were able to synthesize high-grade salts repeatedly by a simple method in the case of TFSA-based salts. The total amount of impurities in each TFSA-based salt was less than 150 ppm, and the amount of water in each salt was less than 100 ppm. Afterwards the effect of anions was examined. Table 1 shows the viscosities and ionic conductivities of the salts of various cations. The salts of all imidazolium-TFSA showed the properties of the ionic liquids at the room temperature. The viscosities at 298 K of AMIm-, AEIm- and DAIm-TFSA were 32, 26 and 28 mPa s, respectively, and almost equal to that of EMIm-TFSA (31 mPa s). In general, the increase in the size of cation in an ionic liquid increases the viscosity. The effect of the ion size was confirmed by the comparison between the viscosities of EMIm-TFSA (31 mPa s) and BMIm-TFSA (52 mPa s). Although DAIm cation was much larger than EMIm cation, the viscosity of DAIm-TFSA (28 mPa s) was lower than that of EMIm-TFSA (31 mPa s). Table 1 also shows the result that the viscosity of

**Table 3**  
Viscosities and ionic conductivities of 1.4 M PC solutions at 298 K.

Salts	Viscosity/mPa s	Ionic conductivity/mS cm <sup>-1</sup>
EMIm-TFSA	4.3	13.5
ATMA-TFSA	5.1	11.4
MTAA-TFSA	6.4	8.8
AMPy-TFSA	5.3	11.0
AMIm-TFSA	5.1	12.5
AEIm-TFSA	4.9	12.2
DAIm-TFSA	5.1	11.3
MVIm-TFSA	5.8	12.6
BTMIm-TFSA	5.4	10.3
TEMA-BF <sub>4</sub>	4.3	14.3
EMIm-BF <sub>4</sub>	3.8	15.3
AMIm-BF <sub>4</sub>	4.2	14.4
DAIm-BF <sub>4</sub>	4.7	13.4

**Table 4**  
Pore structure parameters of activated carbon.

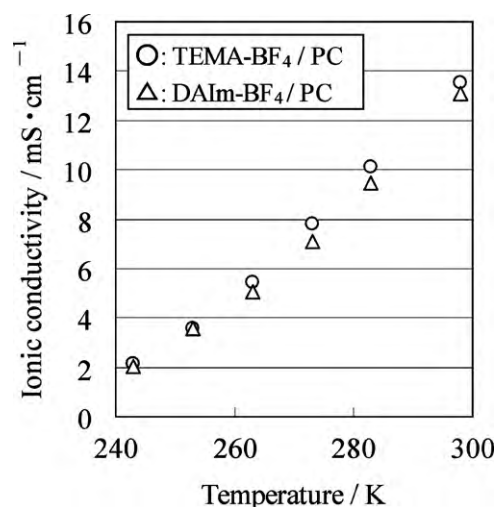
Carbon	Surface area/m <sup>2</sup> g <sup>-1</sup>	Average pore diameter/nm	Average particle size, D <sub>50</sub> /μm
A	2400	1.73	10.8
B	2300	1.82	3.9

BMIm-TFSA is higher than that of EMIm-TFSA suggesting the larger size of cation of BMIm. The discrepancy may be contributed to the plasticizing effect of the allyl group on the *N*-position [23,24]. DAIm-TFSA have the relatively planar structures compared to those of EMIm because of the presence of the double bond having a planar structure [25]. The planar structure may decrease the chance of collision of ions. The similar phenomenon was observed in the result of Py13-TFSA (63 mPa s) and AMPy-TFSA (52 mPa s). The previous study reported that the viscosities of Py13-TFSA, AMPy-TFSA, 1-methyl-1-propylpiperidinium-TFSA and 1-allyl-3-methylpiperidinium-TFSA were 59, 52, 141 and 108 mPa s at 298 K, respectively, and the viscosity of AMPy-TFSA was the lowest in these ionic liquids [25].

The viscosity of BTMIm-TFSA (44 mPa s) was lower than that of BMIm-TFSA (52 mPa s), while the viscosity of MVIm-TFSA (67 mPa s) was higher than that of EMIm-TFSA (31 mPa s) and allylimidazolium-based ionic liquids, AMPy-TFSA, AMIm-TFSA, AEIm-TFSA and DAIm-TFSA (52, 32, 26 and 28 mPa s, respectively). It seems that the functionalization of the butenyl group caused the plasticizing effect, but the vinyl-functionalization caused little effect.

It is also noted that the viscosity of AEIm-TFSA was slightly lower than that of AMIm-TFSA although the former cation was larger than the latter. Generally, the increase of the ionic size leads to the increases in the viscosity as the result of the decrease of the coulomb interaction and the increase of the entanglement of ions. The effect of allyl-functionalization may depend on the length of the alkyl group on the neighboring N atom in the imidazolium ring. Therefore, the detail of the effect may be beyond the classical consideration.

All the ammonium-type salts used in this study are solid at 298 K without regard to the existence of allyl groups. The sizes of TMPA and ATMA are thought to be almost same. TMPA-TFSA is known to be an ionic liquid, while ATMA-TFSA is not an ionic liquid. The melting points of TMPA-TFSA and ATMA-TFSA were reported to be about 290 and 313 K [34]. The difference of the melting points may



**Fig. 1.** Temperature dependence of the ionic conductivities on temperature of 1.4 M TEMA-BF<sub>4</sub>/PC and DAIm-BF<sub>4</sub>/PC electrolytes.

**Table 5**  
Temperature dependence of capacitance of 1.4 M various type salts/PC solutions at 298 and 243 K.

Salts	Structure of a cation	Capacitance/F g <sup>-1</sup>		DC-IR/Ω	
		298 K	243 K	298 K	243 K
EMIm-TFSA		34.1	5.4	10	330
ATMA-TFSA		35.4	2.0	34	680
MTAA-TFSA		34.9	1.9	20	670
AMPy-TFSA		37.2	6.4	13	320
AMIm-TFSA		37.6	8.6	15	270
AEIm-TFSA		37.3	13.5	19	200
DAIm-TFSA		37.5	19.9	13	160
MVIm-TFSA		36.8	1.1	38	950
BTMIm-TFSA		33.5	3.0	13	420
TEMA-BF <sub>4</sub>		33.6	14.5	0	190
EMIm-BF <sub>4</sub>		34.1	25.2	0	110
AMIm-BF <sub>4</sub>		36.0	29.8	0	100
DAIm-BF <sub>4</sub>		36.5	29.6	0	100

be explained by the difference of the electron donation properties of propyl and allyl group to the positive charge of the N-position.

The ionic conductivities of the salts were also shown in Table 1. The conductivities of AMIm-, AEIm-, DAIm-TFSA and AMPy-TFSA, which were allyl-substituted ionic liquids, were 6.7, 7.4, 4.9 and 3.7 mS cm<sup>-1</sup>, and the values were lower than those of the alkyl-substituted ones. From Nernst–Einstein equation and Stokes–Einstein equation, conductivity  $\sigma$  is expressed by the following equation (1):

$$\sigma = \frac{z^2 e_0^2 N}{6V\pi r \eta} \quad (1)$$

where  $z$  is the valence of the charge carrier,  $e_0$  is the elementary charge,  $N$  is the number of charge carriers present in the volume  $V$ ,  $r$  is the effective radius and  $\eta$  is the viscosity. Hence, the conductivity  $\sigma$  is proportional to the number of charge carriers  $N$  and inversely proportional to the viscosity  $\eta$  and the effective radius  $r$ . According to Eq. (1), the decrease in the ionic conductivities of the allylimidazolium-based ionic liquid suggests that the effect of the increase in the effective radius is bigger than that of the decreasing viscosity. The allylimidazolium-based ionic liquids, AMIm-, AEIm- and DAIm-TFSA, showed the higher ionic conductivities than that of BTMIm-TFSA, whose cation size may be relatively large. The size

of MVIm was seemed to be a little smaller than that of the EMIm, but the ionic conductivity of MVIm-TFSA was much lower than EMIm-TFSA. The low ionic conductivity of MVIm-TFSA might be explained by the difference of the structure between ethyl and vinyl groups, which affected the dissociation degree of ionic liquids, but the detail of the effect has not been clarified.

Table 2 shows the properties of BF<sub>4</sub>-based salts. As shown in Table 2, the functionalization of the allyl groups on the N-position increased the viscosity. The similar result was reported previously [26]. A little difference in the effect among the functionalization of allyl groups onto viscosities might depend on the kind of paired anions. The lower ionic conductivities of AMIm- and DAIm-BF<sub>4</sub> compared with EMIm-BF<sub>4</sub> might be caused by the higher viscosities and larger cation of AMIm- and DAIm-BF<sub>4</sub>. In the case of the BF<sub>4</sub>-based ionic liquids as shown in Table 2, AMIm- and DAIm-BF<sub>4</sub> showed much lower ionic conductivities than EMIm-BF<sub>4</sub> and the low conductivities might be caused by the higher viscosities and larger cation of AMIm- and DAIm-BF<sub>4</sub> than those of EMIm-BF<sub>4</sub>.

Table 3 shows the viscosities and ionic conductivities of the electrolytes of various salts and PC solvent. In the case of TFSA-based electrolytes, allylimidazolium (AMIm, AEIm and DAIm)-based electrolytes showed the low viscosities and high ionic conductivities

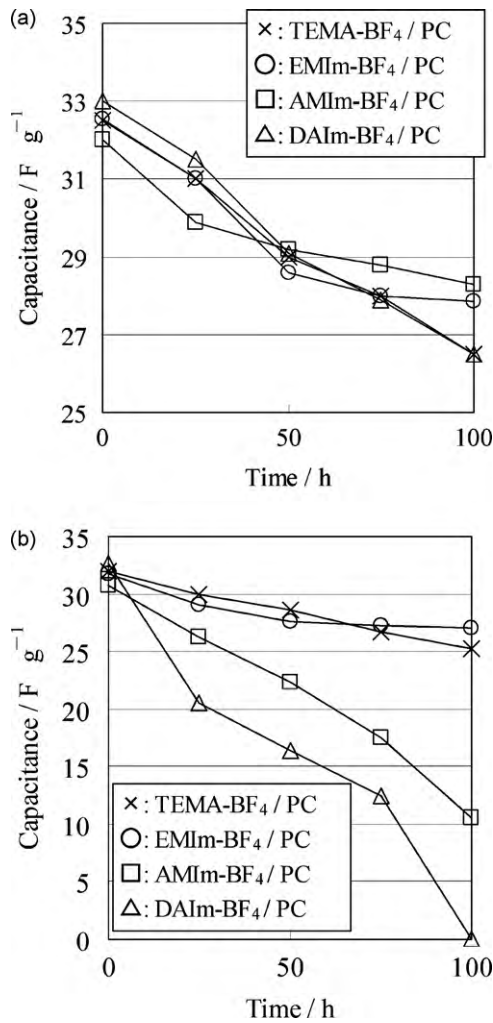


Fig. 2. Capacitances operating at 2.0 V, (a) 298 K and (b) 243 K of various electrolytes during continuous charging at 2.5 V, 333 K for 100 h. The concentration of electrolyte was 1.4 M in PC.

compared to allylammonium and butenylimidazolium. The high viscosities and low ionic conductivities of MTAA-TFSA/PC and ATMA-TFSA/PC electrolytes might be caused by the large cation and the low dissociation. MVIIm-TFSA/PC electrolyte showed the high ionic conductivities in spite of the high viscosity, and the high ionic conductivity may be explained by the small size of MVIIm, which enabled the easy mobility of ions. AMIm-BF<sub>4</sub>/PC and DAIm-BF<sub>4</sub>/PC showed the ionic conductivities comparable to commercially available TEMA-BF<sub>4</sub>/PC electrolyte.

Fig. 1 shows the temperature dependence of ionic conductivity for 1.4 M TEMA-BF<sub>4</sub>/PC and DAIm-BF<sub>4</sub>/PC electrolytes. The ionic conductivity was 10<sup>-4</sup>–10<sup>-3</sup> S cm<sup>-1</sup> at the measured temperatures. It can be seen that the conductivities at low temperature of the electrolytes were almost the same.

### 3.2. Comparison of EDLC capacitance and DC-IR

Table 4 shows the properties of activated carbons studied which have been well established for EDLC performance [35,36]. We properly used two kinds of activated carbons (A: bigger particle size; B: smaller particle size) depending on the situation. In the case of the initial characterization of EDLC, we used activated carbon A which expands the difference of the performances between various electrolytes. In the case of the life test, we used activated carbon B which is able to eliminate the effect of the degradation of activated

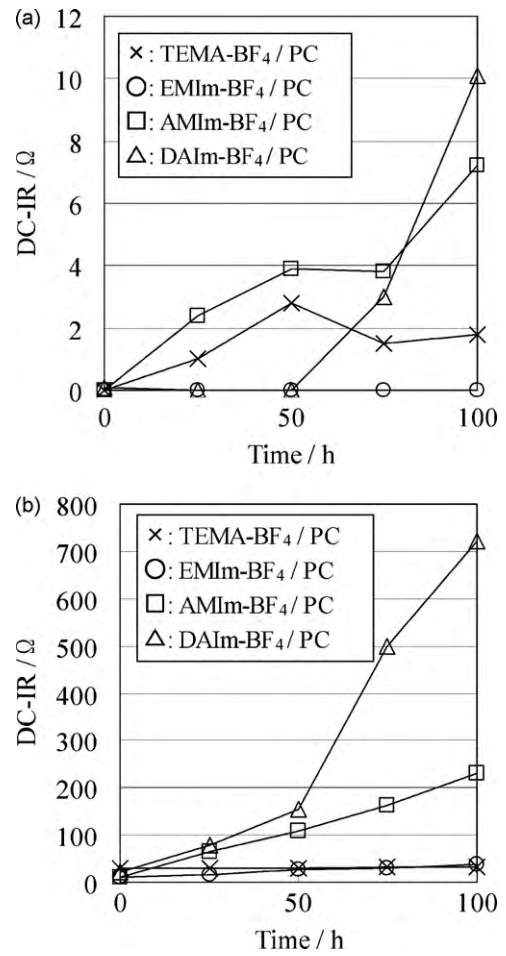


Fig. 3. DC-IRs operating at 2.0 V, (a) 298 K and (b) 243 K of various electrolytes in PC/DMC (1/1, v/v) during the operation of continuous charging at 2.5 V at 333 K. The concentration of electrolyte was 1.4 M.

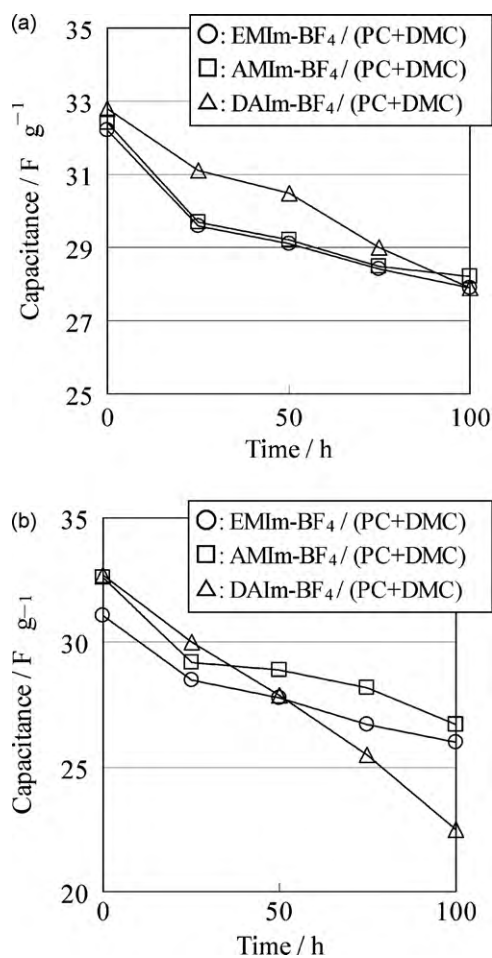
carbon itself and shows the better life performance of EDLC at 2 V, 243–298 K.

Table 5 shows the temperature dependence of the capacitances of 1.4 M various type-electrolytes. We can see that capacitances of allylimidazolium, allylpyrrolidinium, and vinylimidazolium-based electrolytes at 298 K were 36.8–37.6 F g<sup>-1</sup> and higher than those of the others (33.5–35.4 F g<sup>-1</sup>). It is reported that the high concentration carrier on the double-layer structure on the carbon surface and the smaller ions caused the high capacitance [37]. It is also reported that the geometric structure of ions in electrolytes affected on the capacitance, for example, flat ions such as imidazolium might go more smoothly into the micropore and cause the high capacitance [38]. As shown in Table 5, the capacitances of the cells of

Table 6

Viscosities and ionic conductivities of various salts/(PC+DMC) (PC and DMC: 50 vol%) solutions at 298 K. The concentration of salts was 1.4 M.

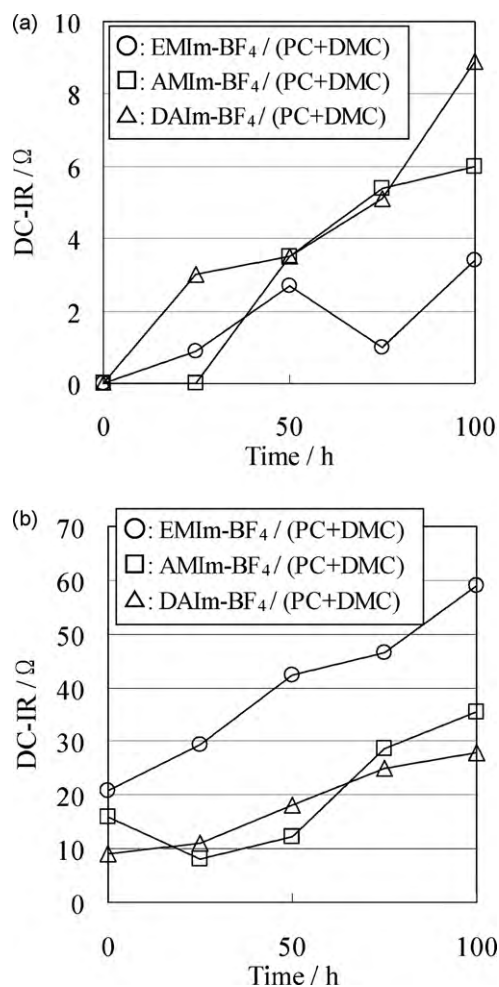
Salt	Solvent	Viscosity/mPa s	Ionic conductivity/mS cm <sup>-1</sup>
EMIm-BF <sub>4</sub>	PC	3.8	15.3
EMIm-BF <sub>4</sub>	PC+DMC	2.3	18.9
AMIm-BF <sub>4</sub>	PC	3.8	15.3
AMIm-BF <sub>4</sub>	PC+DMC	2.4	17.0
DAIm-BF <sub>4</sub>	PC	4.7	13.4
DAIm-BF <sub>4</sub>	PC+DMC	2.9	15.1
DAIm-BF <sub>4</sub>	DMC	1.9	10.1
DAIm-BF <sub>4</sub>	GBL	3.1	16.1



**Fig. 4.** Capacitances operating at 2.0 V, (a) 298 K and (b) 243 K of the various electrolytes including PC/DMC (1/1, v/v) as a solvent after the operation of continuously charging at 2.5 V, 333 K for 100 h. The electrolyte concentration was 1.4 M.

allylimidazolium-based electrolytes were relatively high regardless of the large cation. The ILs with an allyl group and a vinyl group may have relatively planar structures compared to those of ILs with saturated substituent because of the presence of the double bond having a planar structure. Additionally, there may exist some specific interactions between allyl or vinyl-substituted cations and activated carbons, and the interaction such as  $\pi$ - $\pi$  interaction or hydrogen bonding was previously proposed [38].

The other effect of the substitution of allyl groups was observed on the high capacitance at low temperature, 243 K. The high capacitance at low temperature might be caused by some interactions between allyl group and surface functional groups of activated carbon, the supercooling nature of allylimidazolium-TFSA, or the difference of the solvated state of cations. If there had been the interaction between an allyl group and a surface functional group of activated carbon, the interaction would lead to the dense double layer between carbon and electrolyte, and the capacitance would increase. It is previously suggested that there was an interaction between the cellulose hydroxyl oxygen and allylimidazolium, and the interaction might be responsible for the solubility of cellulose to allylimidazolium-based ionic liquid [33]. The similar interaction between allylimidazolium-based ionic liquids and activated carbons possibly exists and the effect on low temperature EDLC performance was thought to be increased by the number of allyl groups. In fact, the EDLC cell of an imidazolium with two allyl groups (DAIm-TFSA) showed the better performance than those of an imidazolium with a single allyl group (AMIm-TFSA and



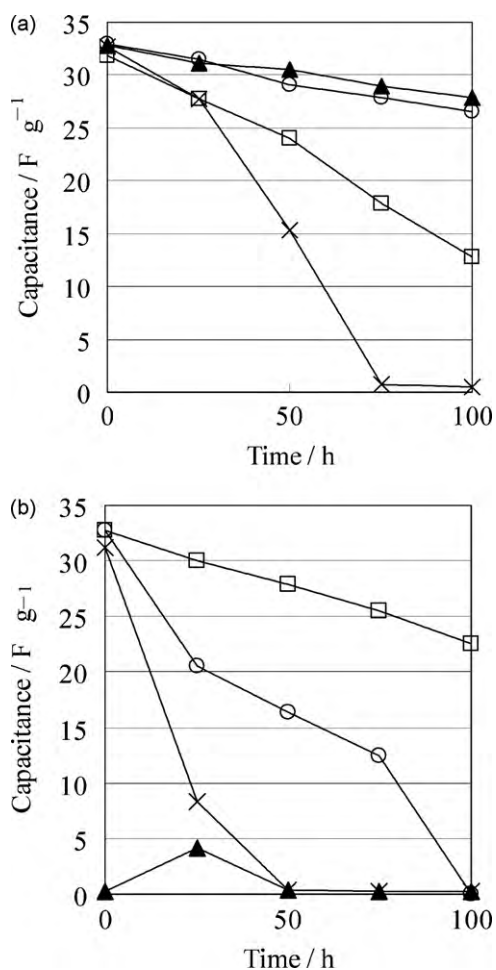
**Fig. 5.** DC-IRs operating at 2.0 V, (a) 298 K and (b) 243 K of the various electrolytes including PC/DMC (1/1, v/v) as a solvent after the operation of continuously charging at 2.5 V, 333 K for 100 h. The electrolyte concentration was 1.4 M.

AEIm-TFSA), and the better performance of DAIm-TFSA suggests that the effects of allyl groups were amplified by the number of allyl groups.

Although DAIm-TFSA showed the best performance at low temperature, the phenomenon was not observed in the case of allylammonium and butenylimidazolium at all. The reason why the improvement was not obtained in the case of ammonium-based electrolytes has not been clarified. The high capacitance at 243 K was not observed in the case of MVIm-TFSA. It seems that an allylimidazolium has a greater tendency to show the planar structure as compared with the other cations; allylammonium, butenylimidazolium and MVIm, and the planar structure particularly lead to the excellent performance of EDLC cells.

The possibility that the supercooling nature leads to the inhibition of precipitation of salts and recombination of a cation and an anion at low temperature should also be considered. The increase in capacitance with allyl-substituted cations may come from the decrease in the effective radius of cation caused by the poor solvation property of allyl group. The relation between the solvated state of ions and capacitance of EDLC cell was previously reported [39,36].

The DC-IR values of the EDLC cells of allyl-functionalized cations (AMPy, AMIm, AEIm and DAIm) and TFSA anion were 160–320  $\Omega$  at 243 K, and were much lower than those of EMIm-, ATMA-, MTAA-, MVIm- and BTMIm-TFSA (330, 680, 670, 950 and 420  $\Omega$  at 243 K, respectively). The result may be also explained by the above-



**Fig. 6.** Capacitances operating at 2.0 V, (a) 298 K and (b) 243 K of DAIm-BF<sub>4</sub> in various solvent during the operation of continuous charging at 2.5 V, 333 K for 100 h. The electrolyte concentration of electrolyte was 1.4 M; (○) PC; (□) PC + DMC; (▲) DMC; (×) GBL.

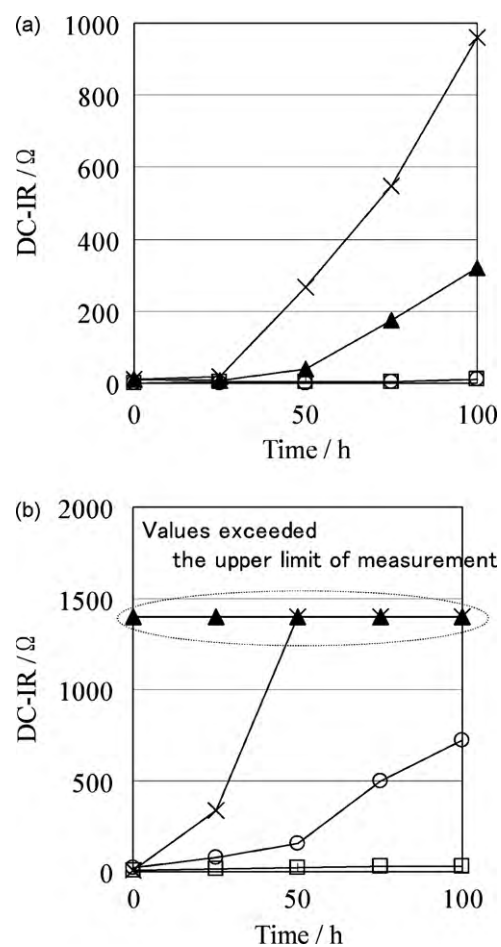
mentioned assumption at the result of the capacitance at the low temperature. DC-IR of DAIm-TFSA was about half of the value of EMIm-TFSA.

In the case of BF<sub>4</sub>, the capacitance at 298 and 243 K decreased in the following order, AMIm-BF<sub>4</sub> = DAIm-BF<sub>4</sub> > EMIm-BF<sub>4</sub> > TEMA-BF<sub>4</sub>. DC-IR values increased in the following order, AMIm-BF<sub>4</sub> = DAIm-BF<sub>4</sub> < EMIm-BF<sub>4</sub> < TEMA-BF<sub>4</sub>. The extent of the effect of allyl group in the case of BF<sub>4</sub> on DC-IR was not so remarkable, comparing with that of the case of TFSA. Thus the extent of the influence of the allyl-functionalization was found to depend on the kind of anion.

### 3.3. The life test of EDLCs of BF<sub>4</sub>-based electrolytes

In contrast with batteries, the cycling test is less important for an EDLC, because mostly the deterioration occurs at the maximum operating voltage. So, as the more useful life test, we continuously operated the cell at 2.5 V, 333 K and then evaluated the capacitances and the DC-IRs operating at 2.0 V, 243–298 K. The activated carbon B shown in Table 4 and BF<sub>4</sub>-based electrolytes were used for the life test. Here, TFSA anion was not used, because TFSA anion causes the corrosion of the Al current collector [40,41], and carbon B was preferred for life test because the cell of carbon A showed too high resistance and insensitive to the deterioration.

The capacitances at 243 and 298 K of 1.4 M electrolytes during 100 h operation are shown in Fig. 2. Fig. 2 shows that capaci-



**Fig. 7.** DC-IRs operating at 2.0 V, (a) 298 K and (b) 243 K of DAIm-BF<sub>4</sub> in various solvent during the operation of continuous charging at 2.5 V, 333 K for 100 h. The electrolyte concentration was 1.4 M; (○) PC; (□) PC + DMC; (▲) DMC; (×) GBL.

tance at 298 K did not depend on the kind of the salts in the case of BF<sub>4</sub>-based electrolytes, and capacitances at 243 K strongly depended on the kind of the salts. The capacitances of AMIm- and DAIm-BF<sub>4</sub> decreased abruptly during the operation suggesting the easy decomposition at 2.5 V, 333 K. The reason of the easy decomposition of AMIm- and DAIm-BF<sub>4</sub> may come from the instability of unsaturated bonds of allylimidazolium cations. However, it was reported that the electrochemical windows of EMIm-BF<sub>4</sub>, AMIm-BF<sub>4</sub> and DAIm-BF<sub>4</sub> were 4.1, 5.4 and 5.8, respectively, and the allyl groups made the anodic limit of the salt higher [26]. The electrochemical windows of the pyrrolidinium- and piperidinium-based ionic liquids were also studied, and the electrochemical windows of 1-methyl-3-propyl-pyrrolidinium, AMPy, 1,1-diallylpyrrolidinium, 1-methyl-1-propylpiperidinium, 1-allyl-1-methylpiperidinium, and 1,1-diallylpiperidinium-TFSA were reported to be 5.6, 5.5, 4.7, 5.2, 5.0 and 4.9 V, respectively [25]. The electrochemical stability of allyl-substituted pyrrolidinium and piperidinium-TFSA were a little lower than those of alkyl-substituted ones. The detail of the effect of allyl groups on the electrochemical window has not been clarified. The order of the capacitance retention after 100 h, TEMA-BF<sub>4</sub> = EMIm-BF<sub>4</sub> > AMIm-BF<sub>4</sub> > DAIm-BF<sub>4</sub>, shows that the degradation of EDLC cells depended on the number of allyl groups, and probably that allyl groups decomposed easily. It is previously reported that the adsorbed EMIm cation on pore wall cannot come out easily from the inside of the micropore probably because of chemical interaction between imidazolium cation and hexagonal

carbon plane [38]. Our result may be supported by the above proposal, and the larger number of allyl group might have a greater tendency to adsorb on the pore wall irreversibly. On the contrary, the degradation of the cells using carbon, which was activated by gas reaction and pore volume was lower than that of carbon A and B, was inhibited and this result may be explained by that the stronger interaction between double bond and carbon occurred in the narrow pore. Fig. 3 shows the DC-IR values at 243 and 298 K of 1.4 M electrolytes during 100 h operation. The increase in DC-IR measured at 298 K was slight in all the electrolytes. The DC-IR values at 243 K of AMIm- and DAIm-BF<sub>4</sub> were much higher than those of TEMA- and EMIm-BF<sub>4</sub>. The result suggests that the decomposition of electrolytes prevented ions forming double layer.

#### 3.4. The effect of solvents on the life test of EDLCs

It is reported that a linear-structure carbonate, dimethylcarbonate (DMC) as a co-solvent improved the EDLC performances [42,43]. Table 6 shows the ionic conductivities and viscosities of the electrolytes of the various salts and solvents. The addition of DMC decreased the viscosities of the electrolytes based on EMIm-, AMIm- and DAIm-BF<sub>4</sub> and increased the ionic conductivities, probably because of the lower viscosity of DMC than those of PC. Then we examined the effect of a co-solvent on the durability of EDLC cells. Figs. 4 and 5 indicate the capacitances and DC-IR values at 243 and 298 K using DMC during 100 h operation. As shown, the addition of DMC improved the retention of capacitance and DC-IR values after 100 h operation. The durability of the cell using allylimidazolium was improved up to that of the cell using EMIm-BF<sub>4</sub>. We need further investigation to clear the detail effect of DMC. The addition of DMC seemed to affect on the solvated state of ions, although it has not been reported that the solvated state of ions influenced on the ability of electrolyte to decompose.

When EMIm-BF<sub>4</sub> was mixed with DMC without PC and stood still for a while, the phase separation occurred. On the other hand, DAIm-BF<sub>4</sub> could dissolve in sole DMC and also sole  $\gamma$ -butyrolactone (GBL). Table 6 shows the viscosities and ionic conductivities of the electrolytes of the various solvents. DMC decreased not only the viscosity but also the ionic conductivity of the electrolyte. The electrolytic dissociation of DAIm-BF<sub>4</sub> salt seemed to be inhibited in DMC solvent. GBL showed the moderate values of the viscosity and ionic conductivity of the electrolyte probably because of the low viscosity and high specific dielectric constant of GBL.

Figs. 6 and 7 indicate the capacitances and DC-IRs at 243 and 298 K of 1.4 M electrolytes during 100 h operation at 2.5 V, 333 K. In the case of DMC, the capacitance at 248 K was very low and DC-IR value exceeded the upper limit of measurement (ca. 1400  $\Omega$ ) even before the operation at 2.5 V and 333 K. The reason of the poor capacitance and extremely high DC-IR of the electrolyte of DMC may be that the electrolyte of DMC freezes at 243 K, because the melting point of DMC is around 276 K. Capacitances at 298 K were comparable to those of DMC + PC solution, but the DC-IR values were much higher than those of PC and PC + DMC solutions. The result suggests that DMC did not improve the durability of EDLC cell of DAIm-BF<sub>4</sub>. In the case of GBL, the degradation after the continuous charging at 2.5 V, 333 K for 100 h was much higher than those of the other electrolytes. For a lithium-ion battery, it is known that GBL readily undergoes the reductive decomposition on the surface of the negative electrodes, forms a solid electrolyte interphase with a high resistance, causing the deterioration of the battery performances [44]. The similar deterioration might occur in the case of GBL for EDLC electrolyte. It is concluded that the selection of solvents strongly affects the degradation of EDLC cells although the detail of the mechanism has not been clarified.

## 4. Conclusions

We synthesized the various TFSA-based ionic liquids of imidazolium and ammonium cations with the saturated alkyl, vinyl, allyl and 1-butenyl groups and examined the properties and EDLC performances of the electrolytes. It was confirmed that the substitution of allyl groups causes the low viscosity compared to saturated alkyl, vinyl and butenyl groups. The low viscosity may come from the plasticizing effect of allyl groups on the N-position, although the effect was not confirmed in the case of BF<sub>4</sub> anion. When the salts were dissolved in PC solvent, the substitution of olefinic groups increased the viscosities of electrolytes compared to the EMIm-based electrolyte. The electrolytes of allyl-functionalized imidazolium showed the better performance at a wide range of temperature particularly in the case of TFSA anion comparing with that of the imidazolium with saturated alkyl, vinyl and butenyl groups and ammonium with allyl groups. The effect of the allyl group on EDLC performance may be explained by the following factor: some interactions between allyl groups and the functional groups on the surface of activated carbon; the supercooling nature of allylimidazolium salts; and the difference of the solvated states of cations. AMIm-BF<sub>4</sub>/PC and DAIm-BF<sub>4</sub>/PC decomposed easily compared to EMIm-BF<sub>4</sub>/PC. The addition of DMC to PC improved the durability of allylimidazolium-based electrolytes. So, the deliberate selection of solvents is important for the durability of EDLC cells.

## References

- [1] J.S. Wilkes, M.J. Zaworotko, *J. Chem. Soc., Chem. Commun.* 965 (1992) 2.
- [2] M. Galiński, A. Lewandowski, I. Stępnik, *Electrochim. Acta* 51 (2006) 5567.
- [3] A. Paul, P.K. Mandal, A. Samanta, *Chem. Phys. Lett.* 402 (2005) 375.
- [4] P. Bonhôte, A.-P. Dias, M. Armand, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* 35 (1996) 1168.
- [5] T. Welton, *Chem. Rev.* 99 (1999) 2071.
- [6] L.A. Balanchard, D. Hancu, E.J. Beckman, J.F. Brennecke, *Nature* 399 (1999) 28.
- [7] H.L. Chum, R.A. Osteryoung, in: D. Inman, D. Lovering (Eds.), *Ionic Liquids*, Plenum Press, New York, 1981.
- [8] K. Tsunashima, M. Sugiyama, *Electrochemistry* 75 (2007) 734.
- [9] J. Sun, M. Forsyth, D.R. MacFarlane, *J. Phys. Chem. B* 102 (1998) 8858.
- [10] H. Sakaebe, H. Matsumoto, *Electrochem. Commun.* 5 (2003) 594.
- [11] C. Arbizzani, M. Biso, D. Cericola, M. Lazzari, F. Soavi, M. Mastragostino, *J. Power Sources* 185 (2008) 1575.
- [12] N. Handa, T. Sugimoto, M. Yamagata, M. Kikuta, M. Kono, M. Ishikawa, *J. Power Sources* 185 (2008) 1585.
- [13] T. Sato, G. Masuda, K. Takagi, *Electrochim. Acta* 49 (2004) 3603.
- [14] M. Ue, M. Takeda, A. Toriumi, A. Kominato, R. Hagiwara, Y. Ito, *J. Electrochem. Soc.* 150 (2003) A499.
- [15] M.M. Islam, M.T. Alam, T. Okajima, T. Ohsaka, *J. Phys. Chem. C* 113 (2009) 3386.
- [16] N. Papageorgiou, Y. Athanassov, M. Armand, P. Bonhôte, H. Pettersson, A. Azam, M. Grätzel, *J. Electrochem. Soc.* 143 (1996) 3099.
- [17] Y. Matsuda, M. Morita, M. Ishikawa, M. Ihara, *J. Electrochem. Soc.* 140 (1993) L106.
- [18] M. Ue, K. Ida, S. Mori, *J. Electrochem. Soc.* 141 (1994) 2989.
- [19] E. Frackowiak, G. Lota, J. Pernak, *Appl. Phys. Lett.* 86 (2005) 64104.
- [20] S. Shiraiishi, T. Miyauchi, R. Sasaki, N. Nishina, A. Oya, R. Hagiwara, *Electrochemistry* 75 (2007) 619.
- [21] J.B. Jones, D.W. Hysert, *Can. J. Chem.* 49 (1971) 325.
- [22] B.K.M. Chan, N. Chang, M.R. Grimmett, *Aust. J. Chem.* 30 (1977) 2005.
- [23] T. Mizumo, E. Marwanta, N. Matsumi, H. Ohno, *Chem. Lett.* 33 (2004) 1360.
- [24] D. Zhao, Z. Fei, T.J. Geldbach, R. Scopelliti, G. Laurenczy, P.J. Dyson, *Helv. Chim. Acta* 88 (2005) 665.
- [25] T. Yim, Y. Lee, H.-J. Kim, J. Mun, S. Kim, S.M. Oh, Y.G. Kim, *Bull. Korean Chem. Soc.* 207 (2007) 1567.
- [26] G. Min, T. Yim, H.Y. Lee, D.H. Huh, E. Lee, J. Mun, S.M. Oh, Y.G. Kim, *Bull. Korean Chem. Soc.* 27 (2006) 847.
- [27] R.P. Swatloski, S.K. Spear, J.D. Holbrey, R.D. Rogers, *J. Am. Chem. Soc.* 124 (2002) 4974.
- [28] S. Zhu, Y. Wu, Q. Chen, Z. Yu, C. Wang, S. Jin, Y. Ding, G. Wu, *Green Chem.* 8 (2006) 325.
- [29] J. Wu, J. Zhang, H. Zhang, J. He, Q. Ren, M. Guo, *Biomacromolecules* 5 (2004) 266.
- [30] N. Hofmann, A. Bauer, T. Frey, M. Auer, V. Stanjek, P.S. Schulz, N. Taccardi, P. Wasserscheid, *Adv. Synth. Catal.* 350 (2008) 2599.
- [31] Z. Fei, D. Kuang, D. Zhao, C. Klein, W.H. Ang, S.M. Zakeeruddin, M. Grätzel, P.J. Dyson, *Inorg. Chem.* 45 (2006) 10407.
- [32] J.-T. Lee, Y.-W. Lin, Y.-S. Jan, *J. Power Sources* 132 (2004) 244.
- [33] H. Zhang, J. Wu, J. Zhang, J. He, *Macromolecules* 38 (2005) 8272.



- [34] H. Matsumoto, M. Yanagida, K. Tanimoto, M. Nomura, Y. Kitagawa, Y. Miyazaki, *Chem. Lett.* (2000) 922.
- [35] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P.-L. Taberna, *Science* 313 (2006) 1760.
- [36] C. Largeot, C. Portet, J. Chmiola, P.-L. Taberna, Y. Gogotsi, P. Simon, *J. Am. Chem. Soc.* 130 (2008) 2730.
- [37] T. Kaneko, M. Watanabe, The 43rd Battery Symposium in Japan, Abstr., 2002, p. 412 (in Japanese).
- [38] S. Shiraiishi, N. Nishina, A. Oya, R. Hagiwara, *Electrochemistry* 73 (2005) 593.
- [39] J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, Y. Gogotsi, *Angew. Chem. Int. Ed.* 47 (2008) 1.
- [40] E.M. Shembel, R.D. Apostolova, A.S. Strizhko, A.I. Belosokhov, A.F. Naumenko, V.V. Rozhkov, *J. Power Sources* 54 (1995) 421.
- [41] X. Zhang, P.N. Ross, J.R. Kostecki, F. Kong, S. Sloop, J.B. Kerr, K. Striebel, E.J. Cairns, F. McLarnon, *J. Electrochem. Soc.* 148 (2001) A463.
- [42] K. Chiba, T. Ueda, H. Yamamoto, *Electrochemistry* 75 (2007) 668.
- [43] M. Ue, M. Takehara, M. Takeda, *Denki Kagaku* 65 (1997) 969.
- [44] S. Kinoshita, M. Kotato, Y. Sakata, M. Ue, Y. Watanabe, H. Morimoto, S. Tobishima, *J. Power Sources* 183 (2008) 755.