Short communication

A novel high temperature stable lithium salt (Li$_2$B$_{12}$F$_{12}$) for lithium ion batteries

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ABSTRACT

Basic properties and battery performances of the novel high temperature stable lithium salt (Li$_2$B$_{12}$F$_{12}$, Dilithium Dodecafluorododecaborate; Li$_2$DFB) were studied using a Mn-based cathode and anode composed of a hard carbon and graphite mixture. The effect of co-solvents (mainly linear carbonate in electrolyte formulation of PC/EC/co-solvent (5/30/65 vol% mixture)) on conductivity, viscosity, charge–discharge capacities, rate performance, temperature performance, cycle life and storage life at 60 °C was investigated. Conductivity of Li$_2$DFB electrolyte increased with reducing its viscosity by changing co-solvent and increasing the volume of the higher dielectric solvent. Li$_2$DFB electrolytes showed comparable discharge capacity and columbic efficiency against LiPF$_6$ electrolyte. Li$_2$DFB electrolytes improved the storage life and cycle life of a Mn-based cell at 60 °C.

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1. Introduction

Improving the life and high temperature stability of lithium ion batteries is a key to realizing their application in EV (electric vehicles), HEV (hybrid electric vehicles) and plug-in HEV [1–3]. There are several factors affecting the battery degradation. These include metal ion dissolution from the cathode material, aluminum dissolution of the current collector, decomposition and deposition of electrolyte on the anode and gas generation from electrolyte decomposition [4,5]. Many approaches have been taken to develop novel electrolyte additives to establish a functional and stable SEI (solid electrolyte interface) films on the electrodes and to protect against undesired reactions. Some examples of additives include VC (vinylene carbonate) [6,7], VEC (vinyl ethylene carbonate) [8,9], VP (vinyl pyridine) [10], LiBOB (lithium bis(oxalato)borate) [11,12], and LiDFOB (lithium difluoro(oxalato)borate) [13]. The SEI film plays an important role to improve the battery life, but it cannot prevent degradation of the bulk electrolyte, especially the lithium salt.

The most commonly used salt in lithium ion batteries, LiPF$_6$ decomposes thermally above 80 °C and generates HF by reaction with residual H$_2$O in organic electrolytes. LiN(SO$_2$CF$_3$)$_2$ and LiN(SO$_2$CF$_2$CF$_3$)$_2$ are thermally stable up to 400 °C and do not react with H$_2$O easily. Thus, these salts were considered to be most promising candidates for overcoming the instability of LiPF$_6$. But, a high reactivity against the cathode has prevented the use of these

compounds as bulk electrolyte salts in commercial lithium ion batteries [14,15]. Many of these salts were based in organic chemistry. We introduced a novel inorganic chemistry based lithium salt, Li$_2$B$_{12}$F$_{12}$, Dilithium Dodecafluorododecaborate; Li$_2$DFB, for lithium battery use. Similar to LiN(SO$_2$CF$_3$)$_2$ and LiN(SO$_2$CF$_2$CF$_3$)$_2$, Li$_2$DFB features good thermal stability up to 400 °C and is chemically and moisture stable. Unfortunately, Li$_2$DFB has an issue of poor conductivity and rate performance relative to LiPF$_6$ due to its large anion size compared to LiPF$_6$. Thus, the study and development of the capable formulations for Li$_2$DFB are needed to introduce it into the industry. This work presents a systematic formulation study of electrolytes containing Li$_2$DFB salt and PC/EC/co-solvent mixtures (5/30/65 vol%) on some physicochemical properties and cell performance including initial charge–discharge capacities, columbic efficiency, rate performance, temperature performance, storage life and cycle life at 60 °C using a Mn-based cathode and a graphite/hard carbon mixed anode cell.

2. Experimental

2.1. Electrolyte preparation conductivity measurement

Li$_2$DFB was synthesized and purified at Air Products and Chemicals, Inc., having more than 99.8% in purity and less than 20 ppm water in dry solid [16]. The Li$_2$DFB was stored in an Ar-filled glove box before use. Battery grade electrolyte solvents and pre-mixed solutions were provided by Kishida Chemical K.K. Electrolytes were prepared by dissolving required amount of lithium salt with pre-mixed solution in a glove box. The electrolytes investigated in this

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Table 1
Studied electrolyte formulations including slat concentration and additives.

Electrolyte	Solvents vol%	Salts mol L^{-1}	Additives wt%
F1 (DMC)	PC/EC/DMC = 5/30/65	Li$_2$DFB = 0.4 LiPF$_6$ = 0.1	VC = 2 PS = 1
F2 (EMC)	PC/EC/EMC = 5/30/65	Li$_2$DFB = 0.4 LiPF$_6$ = 0.1	VC = 2 PS = 1
F3 (DEC)	PC/EC/DEC = 5/30/65	Li$_2$DFB = 0.4 LiPF$_6$ = 0.1	VC = 2 PS = 1
F4 (GBL/DEC)	PC/EC/GBL/DEC = 5/30/30/35	Li$_2$DFB = 0.4 LiPF$_6$ = 0.1	VC = 2 PS = 1
LiPF$_6$ control	PC/EC/DEC = 5/30/65	LiPF$_6$ = 1.27	VC = 2 PS = 1

study are summarized in Table 1. PC (propylene carbonate) and EC (ethylene carbonate) were chosen as high dielectric constant solvents. Four different co-solvent combinations were selected to investigate the formulation effect on electrolyte properties and cell performance, i.e. DMC (dimethyl carbonate), EMC (ethyl methyl carbonate), DEC (diethyl carbonate) and GBL (γ-butyrolactone). A 0.4 M concentration for Li$_2$DFB was chosen to get maximum conductivity. LiPF$_6$ was used an additive for passivating the aluminum current collector. VC (vinylene carbonate) and PS (propane sultone) were added to prevent electrolyte reduction during formation cycling and to form proper SEI (solid electrolyte interface) film [17].

The ionic conductivity of the electrolyte were measured with the formulation did not include the additives using TOA CM 30 V conduct meter at 3 kHz and 25 °C.

2.2. Cell preparation and cell performance evaluations

7 cm × 7 cm size pouch cells were assembled using a cathode composed mainly of lithium manganese oxide, an anode comprised of 50 wt% graphite and 50 wt% hard carbon, and a 25 μm thick polypropylene separator. The cells were charged to 3 V at 0.1C, then kept at open circuit state for 8 h. The cells were then charged up to 4.2 V with 0.2C and kept at 4.2 V for 8 h as constant voltage charging using a TOACAT 3100 battery tester (Toyo system). The rate performance at varying temperature was measured with 0.2, 0.5, 1.0 and 2.0C at 25, 50, 0 and −10 °C. The cells were charged up to 4.2 V for 100% SOC (state of charge) and then stored at 60 °C for storage test. The SOC 100% charge–discharge cycle life test was performed under the condition of 4.2 V charging CC–CV with 1C and 2.7 V discharging with 1C at 60 °C.

3. Results and discussion

3.1. Electrolyte properties

Fig. 1 shows the chemical structure of Li$_2$DFB calculated by molecular orbital method (Spartan, DTF 6-311G base set). Li$_2$DFB has a symmetrical cage structure and possesses two Li ions. This salt needs a two step equilibrium for dissociation as shown in equations (1) and (2) as shown in Fig. 2. This salt is not like other salts used in lithium batteries such as LiPF$_6$ and LiBF$_4$ which have only has one dissociation step. The energy differences (En) between association and dissociation states were estimated from MO calculations as well. The energy E1 for first step dissociation of Li$_2$DFB (126 kcal mol^{-1}) is smaller than the value (E3) for LiPF$_6$ (132 kcal mol^{-1}), indicating that this first step dissociation of Li$_2$DFB is similar to LiPF$_6$. While the energy E2 for second step dissociation of Li$_2$DFB (192 kcal mol^{-1}) is larger than these energy values, indicating that the second step dissociation of Li from Li$_2$DFB is significantly more difficult than the first step dissociation and LiPF$_6$.
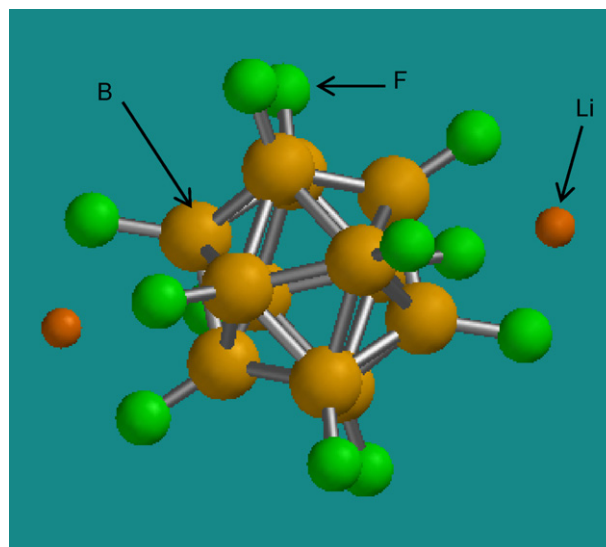

Fig. 1. The structure of Li$_2$DFB salt simulated by MO method.

$$Li_2B_{12}F_{12} \xrightleftharpoons{K_1} Li^+ + LiB_{12}F_{12}^- \qquad E1: 126 \text{ kcal/mol} \quad (1)$$

$$LiB_{12}F_{12}^- \xrightleftharpoons{K_2} Li^+ + B_{12}F_{12}^{2-} \qquad E2: 192 \text{ kcal/mol} \quad (2)$$

$$LiPF_6 \xrightleftharpoons{K_1'} Li^+ + PF_6^- \qquad E1': 132 \text{ kcal/mol} \quad (3)$$
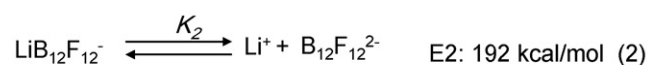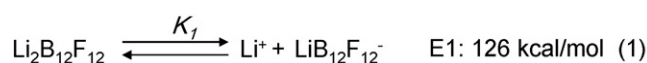
Fig. 2. The equilibrium equations for Li$_2$DFB and LiPF$_6$, energy difference between salt and dissociated state was calculated by MO method.

These considerations suggested that Li$^+$, LiDFB$^-$, and DFB^{2-} must exist and LiDFB$^-$ may be the dominant component in Li$_2$DFB electrolyte.

Fig. 3 shows the conductivity of Li$_2$DFB electrolytes as a function of their reciprocal viscosity. Among the formulations composed of linear carbonate as co-solvent, the conductivity showed good linear relationship to the reciprocal viscosity. Due to the lower molecular weight of the co-solvents F1 (DMC) formulation must have a larger number of co-solvent molecules than other Li$_2$DFB electrolytes. This together with the lowest intrinsic viscosity of DMC, compared with
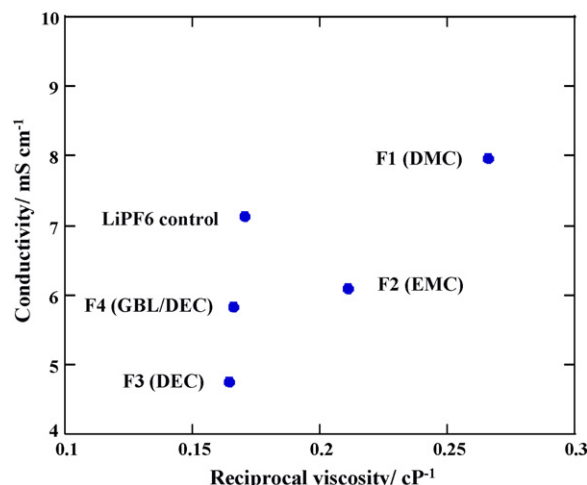

Fig. 3. The conductivity of electrolyte as a function of reciprocal viscosity.

Table 2
Initial charge–discharge capacities and columbic efficiencies.

Electrolyte	Capacity mAh		Columbic efficiency %
	Charge	Discharge	
F1 (DMC)	94.8	70.6	74.5
F2 (EMC)	94.6	71.3	75.6
F3 (DEC)	95.0	70.7	74.4
F4 (GBL/DEC)	94.9	71.1	75.0
LiPF$_6$ control	94.5	71.3	75.5

DEC and EMC contributes to the F1 (DMC) formulation having the lowest viscosity of all of the formulations investigated. That this formulation also has the highest conductivity of all formulations investigated indicates that lowering viscosity is an important consideration for optimizing conductivity with Li$_2$DBF. On the other hand, F4 (GBL/DEC) showed higher conductivity than F3 (DEC) though both had almost the same viscosity. This suggests that GBL increases the dissociation of Li$_2$DBF salt due to its higher dielectric constant. Thus, both viscosity and dissociation are important factors to achieve high conductivity for Li$_2$DBF electrolytes. LiPF$_6$ showed higher conductivity than F4 (GBL/DEC) though both had same viscosity. This fact proved that Li$_2$DBF is less dissociated than LiPF$_6$ as predicted by MO calculation (E2 (192 kcal mol^{-1}) is higher than E3 (132 kcal mol^{-1})), though we should consider the effect of salt concentration for conductivity (LiPF$_6$ formulation had 1.27 M).

3.2. Initial cell performances

Initial charge–discharge performances for all formulations were summarized in Table 2 as an average of five individual cells. Four formulations containing Li$_2$DFB showed comparable charge–discharge capacities and columbic efficiency to LiPF$_6$ control. This suggested that Li$_2$DFB did not undergo significant decomposition during formation cycling. There was no significant difference in initial cell performance among the four different Li$_2$DFB electrolytes. This indicated that the co-solvents did not influence charge–discharge performance at low current rate (0.2C).

Fig. 4 shows the rate performance as a function of relative value of the capacity ([capacity at 2C]/[capacity at 0.2C]) at 25 °C vs. conductivity. At 91.4%, the F1 (DMC) formulation had highest value of all Li$_2$DFB electrolyte formulations, and this value was comparable to the LiPF$_6$ control (91.1%). At 89.2%, the F2 (EMC) formulation also had comparable rate capability to the LiPF$_6$ control. The most viscous F3 (DEC) formulation of Li$_2$DFB had about 10% lower rate
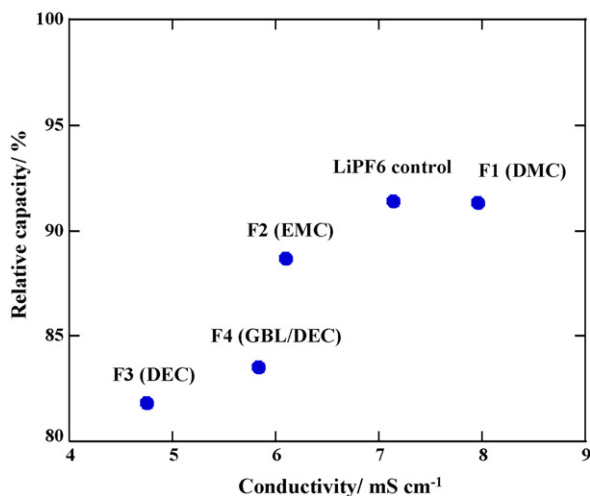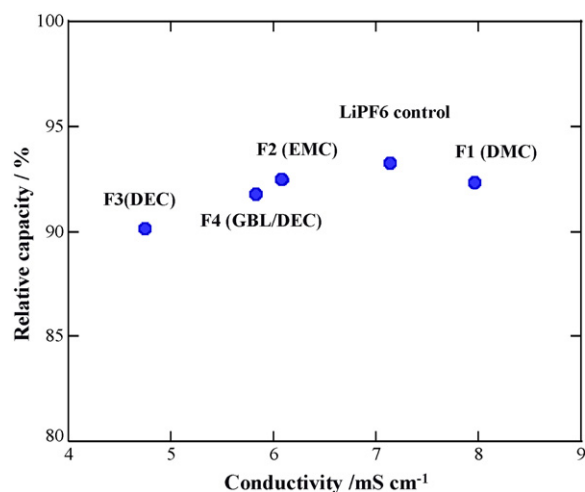
Fig. 5. The relative capacity of −10 °C/25 °C as a function of conductivity for temperature performance with 0.2C rate.

capability by direct comparison with LiPF$_6$ control. Replacing 50% of DEC from this formulation with GBL to give formulation F4 (GBL/DEC) showed significant improvement in rate performance (83.2%). This may be due to the promotion of Li$_2$DFB dissociation by addition of the high dielectric solvent (GBL). The relative capacities were increased by improving the conductivity of electrolyte as expected. This indicates that the rate performance or the resistance of this cell mainly depends upon electrochemical conductivity. It was proven that Li$_2$DFB electrolyte could achieve the comparable rate performance against LiPF$_6$ by selecting solvent formulation.

Fig. 5 shows the temperature performance as a relation between relative value of the capacity ([capacity at −10 °C]/[capacity at 25 °C]) with 0.2C rate. All Li$_2$DFB electrolytes had more than 90% of relative capacities at −10 °C against the capacities at 25 °C, though none of the Li$_2$DFB electrolytes exceeded LiPF6 control (93.3%). This probably was due to the affect of the lower dissociation of Li$_2$DFB than that of LiPF$_6$. The temperature performance also depends on the electrolyte conductivity though the effect is not as large as that for rate performance. This demonstrated that Li$_2$DFB electrolytes had acceptable charge–discharge ability compared to LiPF$_6$, suggesting they kept enough dissociation and viscosity down to −10 °C.

3.3. Battery life performances

Fig. 6 shows the relative capacity change in 4.2 V (100% SOC) storage test at 60 °C. The capacities were measured after 60 °C storage at 0.2C rate and 25 °C. All Li$_2$DFB electrolytes showed very good storage life, compared to LiPF$_6$, retaining more than 80% of initial capacity after 27 days. The F2 (EMC) formulation had the best storage life of all formulations tested, retaining 90% of its initial capacity, while, F1 (DMC) and F3 (DEC) formulations had 81.2% and 83.4% of their initial capacities, respectively. The fact that the F2 (EMC) formulation showed the highest capacity retention was probably due to the balancing the viscosity, conductivity and boiling point, F1 (DMC) and F3 (DEC). Similar better performance with an electrolyte having EMC was found in combination with the non-flammable electrolyte containing MFE (methyl nonafluoro ether), EMC and LiN(SO$_2$CF$_2$CF$_3$)$_2$ [18,19]. The F3 (DEC) formulation, which has same solvent blend and additives as the LiPF$_6$ control, showed much better storage life than the LiPF$_6$ control (62.2% capacity retention). The F4 (GBL/DEC) formulation proved that the replacing 50% of DEC by GBL did not influence the storage life.
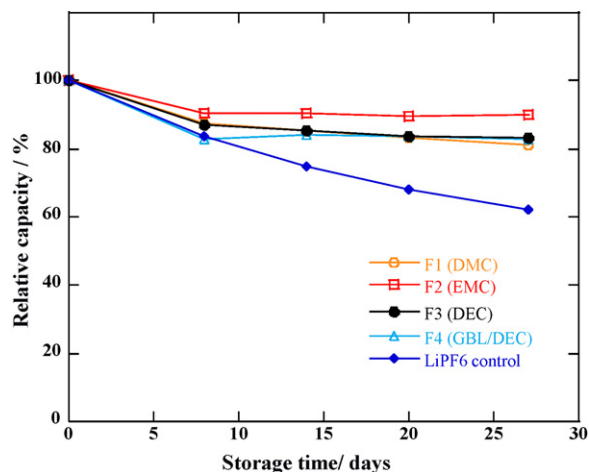
Fig. 4. The relative capacity of 2C/0.2C as a function of conductivity for rate performance at 25 °C.

Fig. 6. The relative capacity change in storage test at 60 °C measured with 0.2*C*.

Fig. 7 shows the relative capacity change in 4.2 V (100% SOC) storage test at 60 °C. The capacities were measured at 1*C* rate and 25 °C after planed storage. All Li$_2$DFB electrolytes showed very good storage life compared to LiPF$_6$ (54.6%), keeping more than 64% of initial capacity after 27 days. The F2 (EMC) formulation still kept 84% of initial capacity at 1*C* rate discharge after 27 days. Though it was a little lower than the capacity measured with 0.2*C* rate, the F2 (EMC) formulation had the best capacity retention in all formulation studied. The F1 (DMC) and F3 (DEC) formulations retained 72.4% and 72.9% of their initial capacities, respectively. It is interesting that the F4 (GBL/DEC) formulation only kept 64% of its initial capacity, though this had the same capacity retention compared to the F1 (DMC) and the F3 (DEC) at 0.2*C* rate. This suggested that the F4 (GBL/DEC) formulation was subject to side reaction on high temperature storage, which increased resistance.

Fig. 8 shows the relative capacity change after 1*C* rate, SOC 100% charge–discharge cycling at 60 °C. With the exception of F4 (GBL/DEC), all Li$_2$DFB electrolytes showed better capacity retention than that of LiPF$_6$ which retained only 35% of its original capacity after 117 cycles. The F3 (DEC) formulation showed highest capacity retention (57.3%) over the same number of cycles. The F1 (DMC) and F2 (EMC) formulations also performed better on high temperature cycling than the LiPF$_6$ control, showing 51% and 49.4% capacity retention, respectively, while the F4 (GBL/DEC) lost the capacity suddenly after approximately 40 cycles. This may be due to the unexpected reaction of GBL during the charge–discharge process.
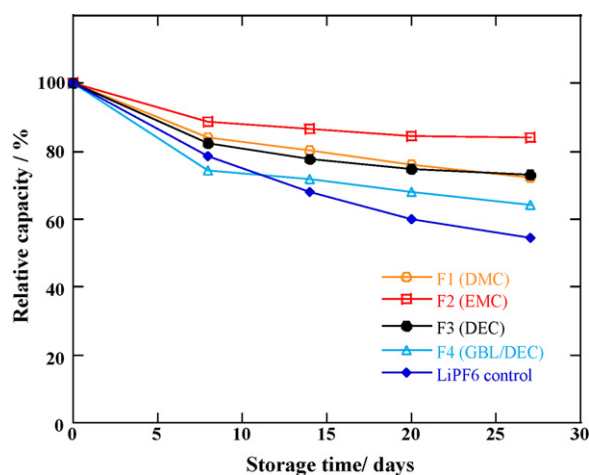

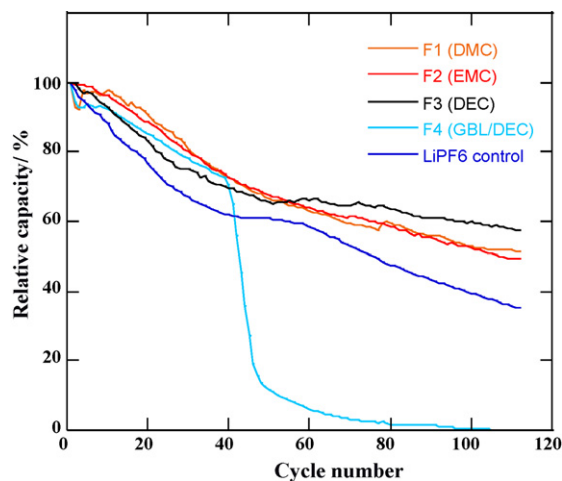**Fig. 7.** The relative capacity change in storage test at 60 °C measured with 1*C*.

Fig. 8. The relative capacity change in 100% SOC 1*C* charge–discharge cycle test at 60 °C.

These storage and cycle life test at high temperature proved the stability and advantage of Li$_2$DFB salt.

4. Conclusions

Physicochemical properties and battery performance of Li$_2$DFB electrolytes were studied to systematically investigate the effects co-solvents. The conductivities of Li$_2$DFB electrolytes depends largely upon their viscosity and can be improved by using small linear carbonates and mixing a high dielectric constant solvent as co-solvent in the PC/EC/co-solvent system. The rate and temperature performance of the Li$_2$DFB electrolyte depended on their conductivity and had comparable performance against an LiPF$_6$ control. The Li$_2$DFB showed better storage and cycle life than the LiPF$_6$ control at 60 °C. These results demonstrate that the Li$_2$DFB is a promising material for improvement of high temperature battery life when used with the appropriate electrolyte formulation and additives.

References

[1] J. Arai, T. Yamaki, S. Yamauchi, T. Yuasa, T. Maeshima, T. Sakai, M. Koseki, T. Horiba, J. Power Sources 146 (2005) 788–792.
[2] Z.H. Chen, K. Amine, J. Electrochem. Soc. 153 (2006) A1221–A1225.
[3] J. Lui, A. Chen, S. Busking, K. Amine, Electrochem. Commun. 9 (2007) 475–479.
[4] K. Amine, J. Liu, S. Kang, I. Belharouak, Y. Hyung, D. Vissers, G. Henriksen, J. Power Sources 129 (2004) 14–19.
[5] K. Araki, N. Sato, J. Power Sources 124 (2003) 124.
[6] J.M. Vollmer, L.A. Curtiss, D.R. Vissers, K. Amine, J. Electrochem. Soc. 151 (2004) A178–A183.
[7] D. Aurbach, J.S. Gnanaraj, W. Geissler, M. Schmidt, J. Electrochem. Soc. 151 (2004) A23–A30.
[8] G. Chen, G.V. Zhuang, T.J. Richardson, G. Lui, J. Philip, N. Ross, Electrochem. Solid-State Lett. 8 (2005) A344–A347.
[9] Y. Hu, W. Kong, Z. Wang, H. Li, X. Huang, L. Chen, Electrochem. Solid-State Lett. 7 (2004) A442–A446.
[10] S. Komaba, T. Itabashi, T. Otsuka, H. Groult, N. Kumagai, B. Kaplan, H. Yashiro, J. Electrochem. Soc. 151 (2005) A937–A946.
[11] K. Xu, S. Zhang, T.R. Jow, Electrochem. Solid-State Lett. 8 (2005) A365–A368.
[12] Z.H. Chen, W.Q. Lu, J. Liu, K. Amine, Electrochim. Acta 51 (2006) 3322–3326.
[13] J. Lui, Z. Chen, S. Busking, K. Amine, Electrochem. Commun. 9 (2007) 475–479.
[14] L.J. Krause, W. Lamanna, J. Schmidt, M. Engle, G. Korba, R. Loch, R. Atanasoski, J. Power Sources 68 (1997) 320.
[15] L. Péter, J. Arai, J. Appl. Electrochem. 32 (2003) 1071.
[16] W.J. Casteel, Jr., S.V. Ivanov, M. Ulman, US Patent 6,781,005 B1 (2004); S.V. Ivanov, W.J. Casteel, Jr., W.H. Bailey, US Patent 7,465,517 (2008); S.V. Ivanov, W.J. Casteel, Jr., G.P. Pez, M. Ulman, US Patent 7,348,103 B2 (2008).
[17] J. Arai, A. Matsuo, Japan patent application No. 2008-335160.
[18] J. Arai, J. Electrochem. Soc. 150 (2003) A219–A228.
[19] J. Arai, J. Power Sources 119–121 (2003) 388–392.