

Conductivity of lithium imide in mixed aprotic solvents for lithium cells

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Abstract

Electrolyte conductivities of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in the single solvents and binary solvent mixtures of propylene carbonate (PC) with methyl acetate (MA), ethyl acetate (EA) or propyl acetate (PA) have been determined at temperatures from -40 to 55 °C. Optimized binary mixed solvent electrolyte solutions were investigated in 23 mm diameter primary Li/MnO₂ button cells at 5 mA/cm^2 . The electrolyte solution $1.25 \text{ M LiN}(\text{CF}_3\text{SO}_2)_2$ in 1:3 (volume ratio) PC:MA gave the highest conductivity as well as the best overall performance in button cells at temperatures from -40 to 55 °C. © 1997 Elsevier Science S.A.

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1. Introduction

The need for improved low temperature performance of lithium cells has required the use of solvents with wide liquidous ranges. It has been found that mixed solvent electrolytes offer high conductivities over the temperature range from about -40 °C to 55 °C [1–3]. The choice of solvents generally includes the use of a high dielectric constant solvent to improve salt solubility, mixed with a low viscosity co-solvent to improve the solution conductivity at low temperatures [2,4,5]. The lithium salt, lithium bis-(trifluoromethanesulfonyl)imide, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ was shown to possess high conductivity in organic solvents [1,6,7]. Ester solvents have been demonstrated to provide significant high rate capability and low temperature performance in lithium rechargeable cells [3,8]. It is therefore the objective of this paper to study the conductivity of the lithium imide salt in MA, EA, and PA and their mixtures with PC, including the performance of the binary mixtures in Li/MnO₂ button cells at a discharge current density of 5 mA/cm^2 , over the temperature range from -40 to 55 °C.

2. Experimental

Propylene carbonate (PC) (Burdick and Jackson) was dried over 4-A size molecular sieves and vacuum distilled. Methyl acetate (MA) (Alfa), ethyl acetate (EA) (Mallinck-

rodt), and propyl acetate (PA) (Aldrich) were dried over 4-A size molecular sieves and fractionated under argon. The lithium imide ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$ salt) (3M) was vacuum-dried at 110 °C overnight. All handling and preparation of the electrolyte solutions were performed in an argon-filled glove box ($\text{ppm H}_2\text{O} < 0.5$). Salt concentrations are reported in molar concentrations and the mixed solvent solutions are reported as volume ratios.

Solution conductivities were measured using a Wayne Kerr Model 6425 precision bridge at 1 kHz in sealed Jones-type conductivity cells ($\kappa \sim 5 \text{ cm}^{-1}$). Cell constants were determined using standard KCl solution. Temperature control for the conductivity and cell studies was provided by a Tenny Jr. environmental chamber. Solvent densities were measured using a Paar Model 45 DMA density meter at 25 °C. Static dielectric constants at 25 °C were obtained using the comparison method [9,10]. Viscosities of the solvents were measured at 25 °C with a Ubbelohde viscometer.

Cathodes were prepared by pelletizing a mixture of 86 wt.% chemical MnO₂ (CDM) (Sadema, 350 °C heat-treated), 5 wt.% KS-44 graphite, 4 wt.% acetylene black carbon, and 5 wt.% Teflon powder. Circular cathode disks having a thickness of 30 mils and a diameter of 1.57 cm were vacuum dried at 60 °C overnight. Lithium anodes were cut from 20 mil thick lithium foil (Foote Mineral) into 1.57 cm diameter disks. Button cells were filled with electrolyte ($\sim 0.33 \text{ g}$) and assembled, as shown in Fig. 1, in an argon-filled glove box ($\text{ppm H}_2\text{O} < 0.5$) and crimp-sealed in a dry room ($< 2\%$ relative humidity). The total cathode weight was 0.33 g with a theoretical capacity of 87.5 mAh based on

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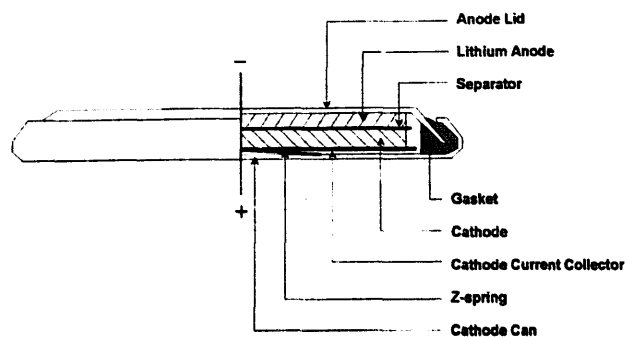


Fig. 1. Button cell assembly, cutaway view.

1 F/mole of MnO_2 . The anode weight was 0.05 g of lithium which was in 2.2 times excess to the theoretical cathode capacity. A single layer of Celgard 2400 was used as the separator. Cells were crimp-sealed using a polyethylene gasket. Details of the cell components are given in Table 1. Cells were discharged at a constant current of 9.68 mA (5 mA/cm^2) using an Amel Model 545 galvanostat–electrometer to a cutoff voltage of 1.5 V at temperatures from -40 to 55°C .

3. Results

In general, the electrolytes in primary lithium cells used to provide low temperature performance are binary solvent solutions containing a high dielectric constant solvent mixed with low viscosity, low dielectric constant solvents. The $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ salt has been considered for use in commercial lithium cells due to its good thermal stability and high conductivity in organic solutions [11]. High conductivity, at low temperatures in $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ electrolyte solutions was reported using mixed solvents of PC with low viscosity ether co-solvents [7]. Low viscosity ester solvents have also been shown to give favorable low temperature performance with LiAsF_6 in rechargeable lithium cells [3,8].

For this study, the conductivity of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in the low viscosity esters MA, EA, and PA and their mixtures with PC was determined. The physical properties of the solvents are given in Table 2. The specific conductivity of solutions as a function of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ concentration at 25°C are shown in Figs. 2 and 3. The solutions containing the more viscous co-solvents EA and PA were found to have lower

Table 2
Solvent properties

Solvent	bp ($^\circ\text{C}$)	fp ($^\circ\text{C}$)	ϵ at 25°C	η at 25°C (cP)	ρ at 25°C (g/cm^3)
PC	241	-49	64.92 ^a	2.53 ^a	1.1995 ^a
PA	102	-95	6.00	0.55	0.8821
EA	77	-84	6.02	0.43	0.8944
MA	56	-98	6.67 ^b	0.36 ^b	0.9279 ^b

^a Ref. [12].

^b Ref. [13].

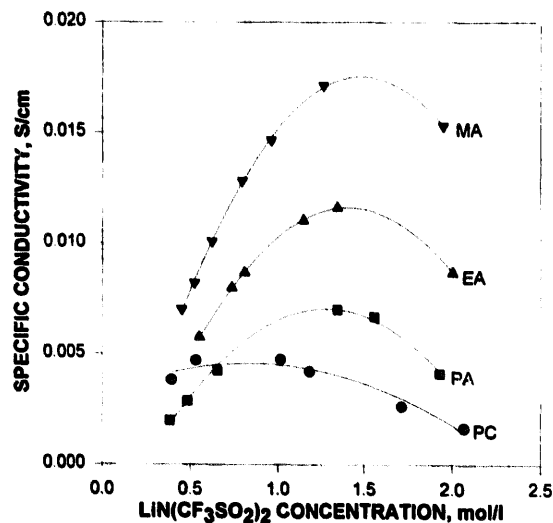


Fig. 2. Conductivity of solutions as a function of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ concentration at 25°C .

conductivities than the MA solutions. Solution conductivities as a function of temperature are given in Figs. 4 and 5 for the optimized salt concentration and solvent ratios. The highest solution conductivity for the binary solvent solutions, over the temperature range from -40 to 55°C was found for 1.26 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in 3:1 MA:PA. Optimized binary solvent solutions for PC in EA and PA were determined by conductivity to be 1.25 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in 17:3 EA:PC and 1.0 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in 3:1 PA:PC.

Although pure MA solutions gave the highest conductivity with $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (from Figs. 2 and 4), they could not be studied in the button cell due to electrolyte leakage. The binary mixed solvent solutions with PC were not found to

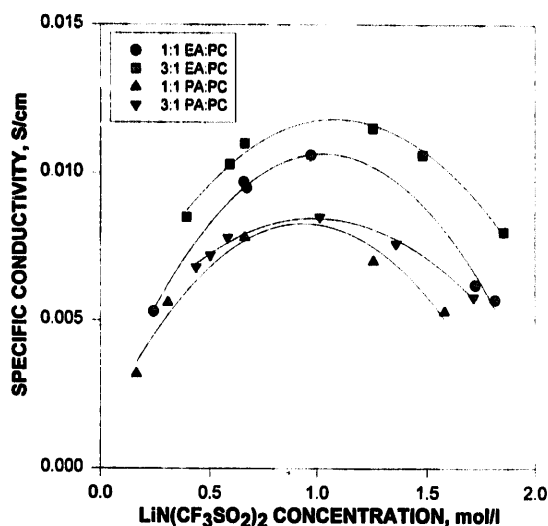
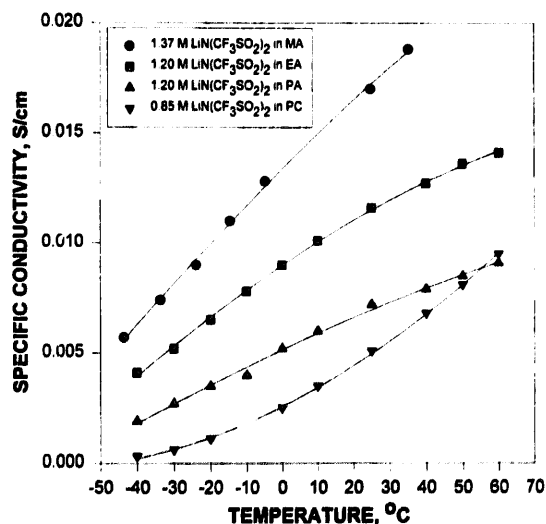
Table 1
Button cell component specifications

Cell diameter (cm)	2.29
Cell height (cm)	0.28
Nominal cell weight (g)	3.3
Cathode can	304 stainless steel
Anode lid	304 stainless steel
Cathode current collector and Z-spring	304 stainless steel
Gasket	polyethylene
Anode	lithium 20 mil thick, 1.57 cm diameter pressed onto a 1.57 cm diameter nickel screen (Exmet 5 Ni 6-3/0A)
Cathode	30 mil thick, 1.57 cm diameter pellet pressed onto a 1.57 cm diameter nickel screen (Exmet 5 Ni 6-3/0A)
Separator	Celgard 2400, 1.90 cm diameter

Table 3

Results for 5 mA/cm² constant current discharge of 23 mm Li/MnO₂ button cells to a 1.5 V cutoff

<i>t</i> (°C)		1.26 M LiN(CF ₃ SO ₂) ₂ in 3:1 MA:PC	1.25 M LiN(CF ₃ SO ₂) ₂ in 17:3 EA:PC	1.00 M LiN(CF ₃ SO ₂) ₂ in 3:1 PA:PC
55	Initial cell OCV	3.40	3.57	3.63
55	Time (h)	6.8	6.9	6.7
55	Capacity (mAh)	66.1	66.8	64.6
55	Cathode utilization (%)	75.5	76.3	73.8
55	Average voltage (V)	2.70	2.68	2.65
55	Cathode energy density (Wh/kg)	541	543	519
25	Initial cell OCV	3.62	3.52	3.62
25	Time (h)	6.7	6.9	5.8
25	Capacity (mAh)	64.9	66.8	55.7
25	Cathode utilization (%)	74.1	76.3	63.6
25	Average voltage (V)	2.64	2.66	2.53
25	Cathode energy density (Wh/kg)	519	538	427
-10	Initial cell OCV	3.60	3.47	3.59
-10	Time (h)	5.2	2.6	1.4
-10	Capacity (mAh)	50.3	25.2	13.6
-10	Cathode utilization (%)	57.5	28.8	15.5
-10	Average voltage (V)	2.32	2.05	2.20
-10	Cathode energy density (Wh/kg)	354	157	91
-30	Initial cell OCV	3.62	3.54	3.64
-30	Time (h)	1.6	0.2	0.05
-30	Capacity (mAh)	15.5	1.9	0.5
-30	Cathode utilization (%)	17.7	2.2	0.6
-30	Average voltage (V)	1.85	2.05	2.20
-30	Cathode energy density (Wh/kg)	87	12	3
-40	Initial cell OCV	3.60	3.52	3.64
-40	Time (h)	0.1	0.05	^a
-40	Capacity (mAh)	1.0	0.48	^a
-40	Cathode utilization (%)	1.1	0.6	^a
-40	Average voltage (V)	2.40	2.05	^a
-40	Cathode energy density (Wh/kg)	7	3	^a

^a Cell could not carry load.Fig. 3. Conductivity of mixed solvent solutions as a function of LiN(CF₃SO₂)₂ concentration at 25 °C.Fig. 4. Conductivity of LiN(CF₃SO₂)₂ solutions as a function of temperature.

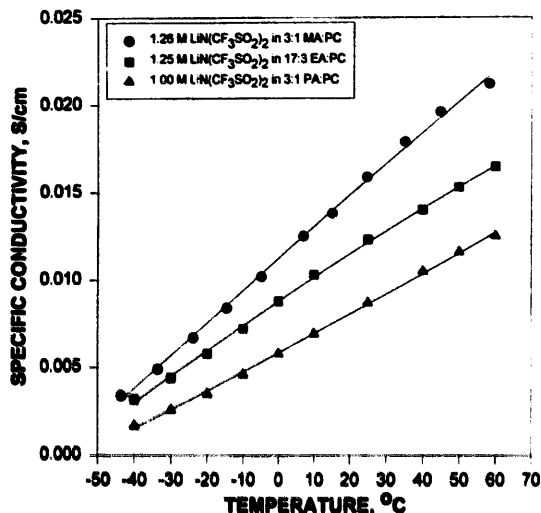


Fig. 5. Conductivity of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in the binary solvent solutions as a function of temperature.

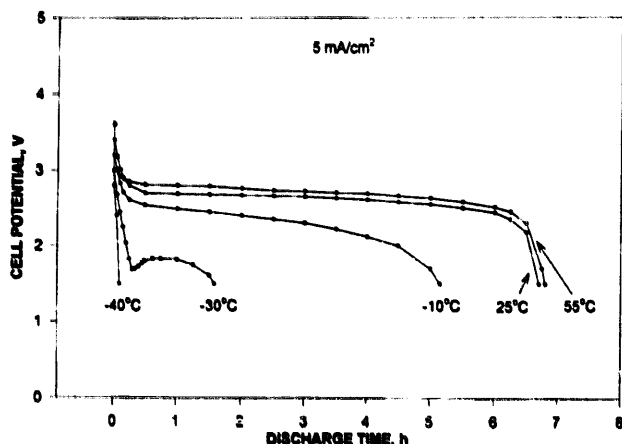


Fig. 6. Discharge polarization curves for $\text{Li}/1.25 \text{ M LiN}(\text{CF}_3\text{SO}_2)_2$ in 1:3 PC:MA/ MnO_2 button cells as a function of temperature.

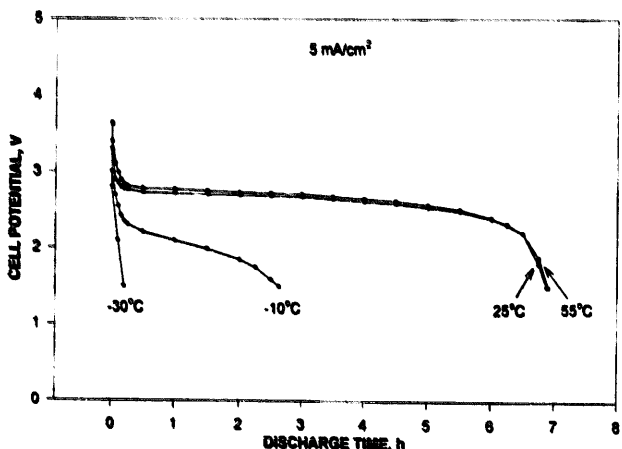


Fig. 7. Discharge polarization curves for $\text{Li}/1.10 \text{ M LiN}(\text{CF}_3\text{SO}_2)_2$ in 3:17 PC:EA/ MnO_2 button cells as a function of temperature.

leak in the button cells over the temperature range studied. Results for the discharges of the Li/MnO_2 button cells are given in Table 3. Cathode energy densities are reported based on the total weight of the cathode, which includes the weight

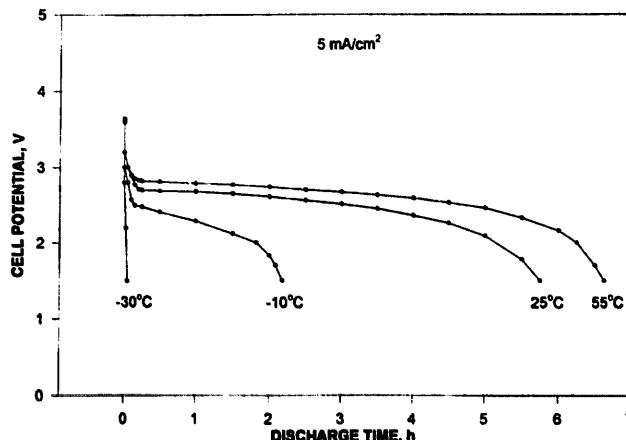


Fig. 8. Discharge polarization curves for $\text{Li}/1.00 \text{ M LiN}(\text{CF}_3\text{SO}_2)_2$ in 1:3 PC:PA/ MnO_2 button cells as a function of temperature.

of the active material, carbons, and binder. Cathode energy densities were generally found to be higher for the more conductive solutions. Cathode utilization was greatest, at low temperatures ($t \leq -10^\circ\text{C}$) for the 3:1 MA:PC solution. Whereas, at high temperatures ($t \geq 25^\circ\text{C}$), higher cathode utilization was obtained with the 17:3 EA:PC solution.

Figs. 6–8 show the voltage polarization curves for the binary solvent electrolytes. Cell capacities were found to be slightly higher for the binary EA–PA solvent solution at temperatures $\geq 25^\circ\text{C}$. At lower temperatures ($< 25^\circ\text{C}$) the MA–PC solutions showed the best performance. Cells containing the PC–PA electrolyte gave reduced cell performance over the more conductive solutions containing EA or MA.

4. Conclusions

Conductivities of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in PC, MA, EA, PA, and the binary solvents MA–PC, EA–PC, and PA–PC were determined. The highest conductivities were found for the solutions containing MA. The $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ electrolyte solutions containing the binary solvents 3:1 MA:PC and 17:3 EA:PC were found to provide good performance in primary Li/MnO_2 button cells over the wide temperature range from -40 to 55°C . The results suggest that $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in the binary solvent solutions of MA–PC and EA–PC may be useful for practical Li/MnO_2 cells.

References

- [1] J.T. Dudley, D.P. Wilkinson, G. Thomas, R. LeVae, S. Woo, H. Blom, C. Horvath, M.W. Juzkow, B. Denis, P. Juric, P. Aghakian and J.R. Dahn, *J. Power Sources*, 35 (1991) 59.
- [2] E.J. Plichta and M. Salomon, *J. Power Sources*, 13 (1984) 319.
- [3] E. Plichta, S. Slane, M. Uchiyama, M. Salomon, D. Chua, W.B. Ebner and H.W. Lin, *J. Electrochem. Soc.*, 136 (1989) 1865.
- [4] S. Tobishima, J. Yamaki and T. Okada, *Electrochim. Acta*, 29 (1984).
- [5] S. Tobishima, J. Yamaki, A. Yamaji and T. Okada, *J. Power Sources*, 13 (1984) 261.

- [6] L.A. Dominey, J.L. Goldman, V.R. Koch and C. Nanjundiah, in S. Subbarao (ed.), *Proc. Symp. Rechargeable Lithium Batteries*, Proc. Vol. 90-5, The Electrochemical Society, Pennington, NJ, USA, 1990, p. 56.
- [7] A. Webber, *J. Electrochem. Soc.*, *138* (1991) 2586.
- [8] E. Plichta, M. Salomon, S. Slane, M. Uchiyama, D. Chua, W.B. Ebner and H.W. Lin, *J. Power Sources*, *21* (1987) 25.
- [9] M. Salomon and E. Plichta, *Electrochim. Acta*, *29* (1984) 731.
- [10] M. Salomon and E. Plichta, *Electrochim. Acta*, *30* (1985) 113.
- [11] L.A. Dominey, V.R. Koch and T.J. Blakley, *Electrochim. Acta*, *37* (1992) 1551.
- [12] M. Salomon and E. Plichta, *Electrochim. Acta*, *28* (1983) 1681.
- [13] M. Salomon, S. Slane, E. Plichta and M. Uchiyama, *J. Solution Chem.*, *18* (1989) 977.