

LiAsF₆ IN PROPYLENE CARBONATE-ACETONITRILE FOR PRIMARY LITHIUM BATTERIES

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(Received March 15, 1982)

Summary

1M LiAsF₆ in 50% v/v propylene carbonate-acetonitrile (PC-AN) is an electrolyte solution which offers improved cathode utilization, improved energy efficiency and more stable discharge voltages when used in primary lithium batteries with MnO₂, TiS₂, Cu₂S, CuS, MoO₃, V₂O₅, V₆O₁₃ and NbSe₃ cathodes. Incorporation of solvated Li⁺ into the cathodic material may be part of the cathodic process, and the lower viscosity and lower molar volume of acetonitrile, which is a solvator of Li⁺ in PC/AN mixtures, are thought to be responsible for the major improvement over LiAsF₆ in PC as electrolyte solution for these cells.

Introduction

Only a few electrolyte solutions are suitable for lithium batteries. Solutions containing acetonitrile (AN) offer the advantage of a component of low viscosity (0.341 cP), high dielectric constant (36.02) and fair solvating properties for lithium salts of large polarizable anions [1, 2]. Thus, highly conducting concentrated solutions of LiClO₄ or LiAsF₆ can be prepared in solutions containing acetonitrile [3]. However, the solutions are usually unsuitable for lithium batteries in one vital respect — acetonitrile reacts readily with lithium unless a third component, such as SO₂, is present to form a protective but conducting film on the lithium [4].

Despite the reaction of acetonitrile with lithium in most of its solutions [3, 4], we found that a solution of 1M LiAsF₆ in high purity propylene carbonate-acetonitrile (PC/AN) containing up to 60% v/v acetonitrile [3] gives no visible indications of reaction with lithium over 6 months at ambient temperatures of 18 - 33 °C. As noted, LiAsF₆ solutions containing more than 60% v/v AN react slowly with lithium [3].

It is known that LiAsF₆ protects lithium better than does LiClO₄ [5 - 7] in many solvents and that addition of PC to AN [4] provides partial protec-

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tion for lithium from the AN, but both LiAsF_6 and PC are needed to provide adequate protection for the lithium in the presence of acetonitrile [3]. Thus 1M LiClO_4 in 50% v/v PC/AN reacts readily (colour changes) with lithium over a few hours, as does 1M LiAsF_6 in acetonitrile (2 days) [3] or, as we have shown in this work, in 50% v/v AN-1,2-dimethoxyethane (AN/DME).

There have been extensive studies of primary and secondary lithium batteries incorporating a variety of cathodes capable of intercalating lithium such as CuS , Cu_2S , MoO_3 , V_2O_5 , V_6O_{13} , NbSe_3 , TiS_2 and MnO_2 [8 - 10]. They are used as porous materials. As noted by Trumbore [9], the effect of the electrolyte solution on the performance of these cathodic materials is a factor which must be considered along with iR effects, films, and polarization at the lithium anode. Nikolskaya *et al.* [11] feel that the cathodic materials incorporate solvated Li^+ ions. If so, then the composition of the solvation shell of Li^+ will be a factor in determining the solvent effect on the cathode performance.

Solvent incorporation has been noted for different solutions at NbSe_2 [11] and for LiClO_4/PC at an NbSe_3 electrode [9] and can lead to rupture of the cathodic material. In PC/AN mixtures the Li^+ solvation shell will be composed of both PC and AN because both AN and PC are similar strong solvators of Li^+ , *i.e.*, $\Delta G_{\text{tr}} \text{Li}^+$ from PC to AN is $+6 \text{ kJ mol}^{-1}$ [1]. In PC the Li^+ solvation shell, of course, only contains PC. Since PC, DME and AN have very different molar volumes and viscosities, the behaviour of intercalation cathodes in LiClO_4/PC may be different from that in $\text{LiAsF}_6/\text{PC}/\text{AN}$ or $\text{LiAsF}_6/\text{PC}/\text{DME}$.

This paper compares the performance in closely similar primary cells containing lithium anodes with each of the eight cathodes noted above, in LiAsF_6/PC , $\text{LiAsF}_6/\text{PC}/\text{DME}$ or $\text{LiClO}_4/\text{PC}/\text{DME}$ and $\text{LiAsF}_6/\text{PC}/\text{AN}$ as the electrolyte solution.

Experimental

Acetonitrile (AN) and propylene carbonate (PC) were purified as described previously [3]. 1,2-Dimethoxyethane (DME) (BDH, England) was refluxed over sodium for 3 h and then distilled over sodium under an argon atmosphere. LiAsF_6 (USS Agrichemicals) and LiClO_4 (ICN, 99.8% pure) were used as received. V_2O_5 (Hopkin and Williams, England) and MnO_2 (Ajax Chemicals, Sydney) were laboratory grade; MoO_3 was Analar grade (Univar, Sydney) and TiS_2 [12], V_6O_{13} [13], CuS and Cu_2S [14], NbSe_3 [15] were prepared by standard procedures.

Solutions were prepared and electrochemical measurements were performed in a recirculating atmosphere of high purity dry argon in a Lintott (Sussex, England) dry box equipped with molecular sieves, P_2O_5 and a VAC HE-493 (Hawthorne, USA) regeneration system. Moisture content was less than 10 ppm and oxygen was less than 1%.

The cell was a polypropylene cylinder with two bronze end screws compressing the various layers of materials all of formal area 1 cm^2 . The layers

were a nickel metal disc, a glass filter paper disc, wet with solvent, as separator, a disc of lithium foil as anode and a nickel gauze disc.

The active cathode material (0.1 - 0.3 g) was ground to a powder with 10% w/w Teflon powder as binder and 10% w/w nickel powder to assist conductivity. Before mixing, all components were sieved through a 15 μm screen. The layer of cathode material was 0.7 - 1.5 mm thick and was compacted against the nickel metal disc in the cylinder with an iron rod. The separator was wetted with 0.5 ml of solvent and after 15 min the brass screws were tightened until the first, firm resistance was felt. The cell was left on open circuit for 10 - 16 h with periodic minor adjustment of the screws to give a maximum OCV value. It was then discharged at the appropriate current density through a PAR Model 173 galvanostat-potentiostat.

The viscosity of the solvents was measured with a synchroelectric viscometer (Brookfield, USA), the density with a digital precision density meter (A. Paar, Austria) and the electric conductance with a digital conductivity meter type G46 (Automated Lab. Equip., Australia). The energy efficiency was calculated by integration under the voltage-time curve.

Results and discussion

The classical electrolyte solution for lithium batteries is 1M LiClO_4 in propylene carbonate (PC) and this is used in much of the published work [8]. More recently, solutions of LiAsF_6 in PC/DME and in PC have gained in popularity [16]. Such electrolytes are compared with PC/AN in Table 1. The conductance of 1M LiAsF_6 in mixtures of PC with AN and with DME at 25 $^\circ\text{C}$ are shown in Fig. 1. As can be seen, 1M LiAsF_6 in 50% PC/AN provides a more highly conducting, less dense, less viscous solution than its competitors of Table 1. The PC/AN mixture has an acceptable liquid range, the lithium salt is adequately soluble, and because of the high dielectric constant it is a strong electrolyte.

We find that lithium is compatible with all three solvents over at least 3 months. The high conductance of the AN-containing electrolyte offers obvious advantages over 1M LiClO_4 or LiAsF_6 in PC.

We have compared the effects on cathode utilization and cell polarizations of LiAsF_6 in PC, in 50% v/v PC/AN and in 50% v/v PC/DME by using the one cell under otherwise identical conditions for each cathode material. The cells contain a large excess of lithium and so are limited by the quantity of cathode material present. Table 2 shows the coulombic and energy utilization of V_6O_{13} , V_2O_5 , MoO_3 , MnO_2 , Cu_2S , CuS and TiS_2 as cathodes in primary lithium cells containing 1M LiAsF_6 in PC, in PC/AN and in PC/DME. In most cases, under the same conditions with LiAsF_6 , the 50% v/v PC/AN electrolyte gives the greatest energy density and greatest coulombic efficiency and the 50% v/v PC/DME is usually better than PC [10]. The advantages of 50% v/v PC/AN are perhaps most marked with V_2O_5 [8, 24] and V_6O_{13} [13, 23] as cathodes. With V_6O_{13} , coulombic efficiencies of 63 - 70% and energy

TABLE 1

Properties of solvents and solutions for lithium batteries at 25 °C

	Solvent				
	PC	AN	DME	PC/AN 50% v/v	PC/DME 50% v/v
Density (g cm^{-3})	1.1995 ^a	0.7767 ^b	0.8622	0.9904	1.0203
Viscosity, η (cP)	2.530 ^c	0.341 ^c	0.455 ^d	1.10	0.85 ^{e, f}
Dielectric constant, ϵ	64.9 ^g	36.02 ^b	7.20 ^d		42 ^{e, h}
Molar volume ($\text{cm}^3 \text{mol}^{-1}$)	85.11	52.85	104.52		

	1M LiAsF ₆ solution				
	PC	AN	DME	PC/AN 50% v/v	PC/DME 50% v/v
Density (g cm^{-3})	1.3196	0.9327		1.1287	1.15 ⁱ
Viscosity, η (cP)	4.80	0.85		2.20	2.35 ^{e, f, i}
Conductance, λ ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	6.0	48.0		21.0	16.2

a. Ref. 17.

d. Ref. 20.

g. Ref. 21.

j. 1M NaClO₄.

b. Ref. 18.

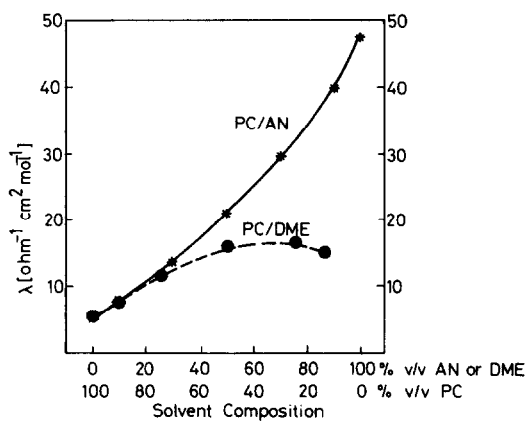
e. Ref. 16.

h. At 20 °C.

c. Ref. 19.

f. At 30 °C.

i. Ref. 22.

Fig. 1. Conductance of 1M LiAsF₆ in PC/AN and in PC/DME [16] mixtures at 25 °C.

densities of 0.67 - 0.71 Wh g^{-1} at 1.6 V cut off voltage, are obtained in LiAsF₆/PC/AN at 1 - 2 mA cm^{-2} . Thus this is a most attractive cathode-electrolyte combination for lithium batteries [13]. With MoO₃ as cathode [25], PC/AN and PC/DME show comparable behaviour as solvents, although at slightly different current densities MnO₂ cells [8, 26] in PC/AN have much lower open circuit voltages (2.75 V) than in PC (3.5 V) or PC/DME (Table 2).

TABLE 2

Capacities of Li/MX cells in 1M LiAsF₆ solvents at 25 °C^a; voltage cut off 1.6 Vⁱ

Cathode MX	Solvent (v/v %) 50/50	Current density (mA cm ⁻²)	OCV (V)	Capacity ^b					
				Theory 10 ³ Q (c kg ⁻¹)	Found 10 ³ Q (c kg ⁻¹)	Theory 10 ³ kJ kg ⁻¹	Found 10 ³ kJ kg ⁻¹	Coul. eff. (%)	Energy eff. (%)
MnO ₂ ^c	PC/AN	2.0	2.75	2218	> 900	6.1	> 2.2	> 40	> 35
	PC/DME ^f	2.0	3.56		650	7.9	1.9	29	24
	PC	2.0	3.51		790	7.8	1.5	36	20
	PC/AN	5.0	2.75		1010	6.1	1.8	45	30
	PC	5.0	3.51		790	7.8	1.5	36	19
TiS ₂ ^d	PC/AN	1.0	2.56	860	500	2.4	1.2	59	50
	PC	1.0	2.53		540	2.2	1.1	63	50
V ₂ O ₅ ^{d, g}	PC/AN	1.0	3.32	530	470	1.8	1.4 ^g	89	78
	PC/DME ^f	1.0	3.22		320	1.7	0.9 ^g	60	53
	PC/AN	2.0	3.32		430	1.8	1.1 ^g	81	61
	PC	2.0	3.22		320	1.7	0.8 ^g	60	47
V ₆ O ₁₃ ^e	PC/AN	1.0	3.22	1500	940	4.8	2.5	63	52
	PC	1.0	2.95		650	4.4	1.3	43	30
	PC/AN	2.0	3.22		1040	4.8	2.3	69	48
	PC/DME	2.0	3.20		790	4.8	1.9	53	40
MoO ₃ ^c	PC/AN	1.0	2.78	1340	1080	3.7	2.6	80	70
	PC	1.0	2.74		> 500	3.7	> 1.2	> 38	> 32
	PC/AN	2.5	2.78		1010	3.7	2.0	75	54
	PC/DME ^f	2.0	2.62		1150	3.5	2.3	86	66
	PC	2.0	2.74		220	3.7	0.4	16	11
Cu ₂ S ^{c, j}	PC/AN	2.0	2.31	1217	790	2.8	1.3 ^j	65	46
	PC/DME	2.0	—		790	2.8	1.2 ^j	65	43
	PC/DME ^f	2.0	—		610	2.8	0.9 ^j	50	32
	PC	2.0	—		470	2.8	0.7 ^j	39	25
CuS	PC/AN	2.0	2.91	2023	360	5.9	0.8	18	14
	PC/DME	1.0	3.32		500	6.7	1.1	25	16

a. Duplicates agreed to within ± 5%.

b. Excess lithium, based on weight of MX.

c. 2 electrons and 2 Li per MX.

d. 1 electron and 1 Li per MX.

e. 8 electrons and 8 Li atoms per MX.

f. 1M LiClO₄.

g. Voltage cut off 2.0 V.

h. Voltage cut off 1.3 V.

i. Unless stated otherwise.

However, the voltage drop of Li/MnO₂ in a PC/AN electrolyte as discharge proceeds at high current densities is very much less in PC/AN than in PC/DME or PC (Fig. 2). Thus, to a cut-off point of 1.6 V, the coulombic efficiency and energy density are greatest for PC/AN (Table 2), making this a useful solvent for Li/MnO₂ batteries, especially at high current densities.

We are unable to account for the much lower OCV of Li/MnO₂ cells in PC/AN compared with PC, but it seems that the AN solvated Li⁺ is interacting with the MnO₂ in a different way from Li⁺ ions solvated by PC.

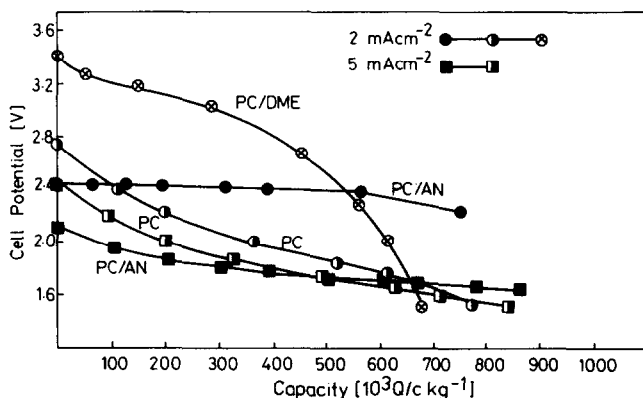


Fig. 2. Discharge curves for Li/MnO₂ cells discharged at 2 or 5 mA cm⁻² in 1M LiAsF₆ PC or PC/AN 50% v/v and in 1M LiClO₄ PC/DME 50% v/v at 25 °C.

Typical discharge voltage–utilization curves (reproducible to $\pm 3\%$ of voltage) at various current densities confirm the substantial advantage of LiAsF₆ 50% v/v PC/AN over LiAsF₆/PC and its smaller advantage over LiAsF₆ or LiClO₄ in 50% v/v PC/DME. Figure 2 shows the improved discharge characteristics at 2 and 5 mA cm⁻² of a Li/MnO₂ cell [26] in 50% v/v PC/AN over 50% v/v PC/DME and PC, with LiAsF₆ as solute.

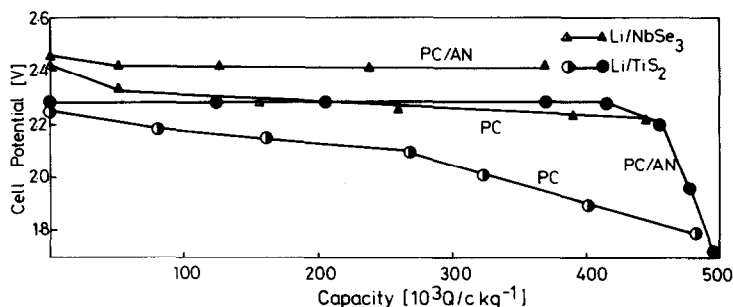


Fig. 3. Discharge curves for Li/NbSe₃ and for Li/TiS₂ cells discharged at 1 mA cm⁻² in 1M LiAsF₆ in PC or in 50% v/v PC/AN at 25 °C.

Figure 3 shows a partial discharge of Li/NbSe₃ [15] and Li/TiS₂ cells at 1 mA cm⁻². The energy efficiency is greater and the voltage more constant up to utilization of at least 0.10 A h g⁻¹ of NbSe₃ in PC/AN than in PC. Figure 4 confirms that Li/V₂O₅ [24] and Li/V₆O₁₃ [13] cells in 50% v/v PC/AN outperform the same cells in 50% v/v PC/DME or PC at a discharge current of 2 mA cm⁻². This is true only after the first two lithium atoms are incorporated in the V₆O₁₃. The same cell, even when discharged in PC at 1 mA cm⁻², gives a very inferior performance to PC/AN at 2 mA cm⁻². Figure 5 (Li/MoO₃ [25]) and Fig. 6 (Li/CuS and Li/Cu₂S [27]) confirm that LiAsF₆ in PC/AN is a much superior electrolyte to LiAsF₆ in PC. The advantage is only marginal for PC/AN over PC/DME for MoO₃ and Cu₂S, but as seen in

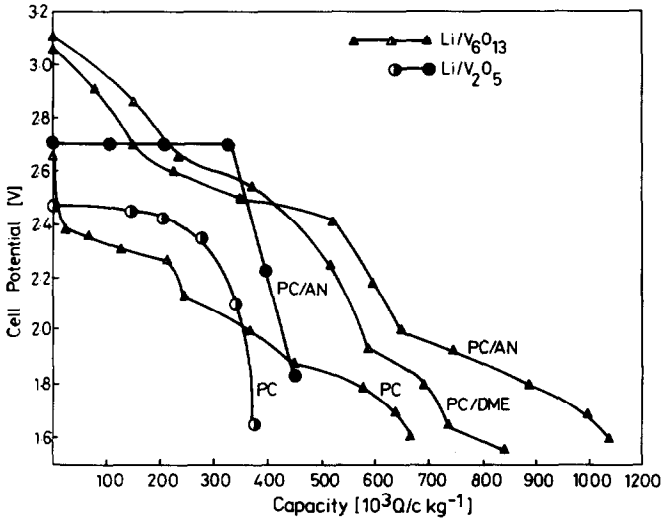


Fig. 4. Discharge curves for $\text{Li}/\text{V}_6\text{O}_{13}$ and for $\text{Li}/\text{V}_2\text{O}_5$ cells discharged at 2 mA cm^{-2} * in 1 M LiAsF_6 in 50% v/v PC/AN or PC/DME and in PC at 25°C .
* $\text{Li}/\text{V}_6\text{O}_{13}$ cell in PC discharged at 1 mA cm^{-2} .

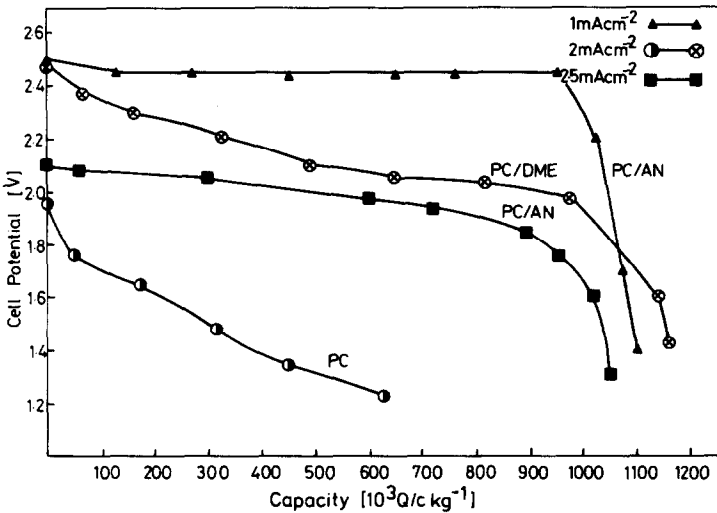


Fig. 5. Discharge curves for Li/MoO_3 cells in PC and in 50% v/v PC/AN or PC/DME containing 1 M LiAsF_6 , discharged at 1, 2, or 5 mA cm^{-2} at 25°C .

Table 2 and Figs. 2 and 4, the PC/AN does show its superiority over PC/DME with MnO_2 , V_2O_5 and V_6O_{13} as cathodes, mainly in terms of better utilization of the cathode material. With Cu_2S , 1 M LiAsF_6 is superior to LiClO_4 in PC/DME.

Because the relative advantage of PC/AN over PC or PC/DME varies with the nature of the cathode material at the same current density, its superiority cannot be only due to greater conductivity or effects at the

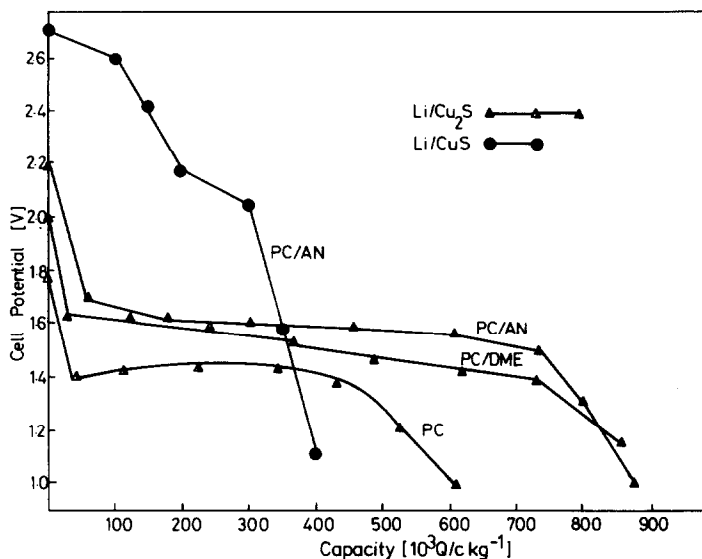


Fig. 6. Discharge curves for Li/Cu₂S and for Li/CuS at 2 mA cm⁻² in PC and in 50% v/v PC/AN or PC/DME containing 1M LiAsF₆, at 25 °C.

lithium anode [3], it must, in part, be due to cathode-solvent interactions, which influence polarizations at the cathode and the utilization of cathode material for incorporation of lithium atoms [11].

Nikolskaya and Tikhonov [11] have shown that almost twice as much lithium is intercalated into NbSe₂ at acceptable potentials from LiClO₄ in acetonitrile as in propylene carbonate. They believe that solvated Li⁺ enters the NbSe₂ and that the electrochemical rate of reduction at an NbSe₂/Li⁺ cathode depends on the solvation energy of Li⁺, being fastest in the least solvating solvent (AN). This observation is of little value if AN reacts with lithium, as is usually the case, but the special features of LiAsF₆/PC/AN [3] allows one to use the superior intercalating properties of AN solvated Li⁺ over PC solvated Li⁺. Similar explanations were advanced to explain the improved performance of Li intercalation into MoO₃ in methylformate over PC [25].

We believe that poor solvation of Li⁺ is not the only factor in determining the advantages of AN as a solvent for intercalation cathodes. Molar volume and viscosity are also relevant. Clearly, AN-solvated Li⁺ is more readily and more rapidly incorporated reductively into many layered cathodes with less disruption of the layers than is the case with PC-solvated Li⁺. Layer disruption by the bulkier DME-solvated Li⁺ is only a little greater than with AN-solvated Li⁺, except for intercalation into MnO₂, where DME gives poor utilization of this material.

Two factors must be considered. Firstly, the effect of solvent on the rate of the reduction process and, hence, the polarization. Secondly, the effect of solvent on lattice disruption and, hence, utilization of cathode material and its cyclability. The relatively poor cation solvating properties of

AN, its lower viscosity and its smaller molar volume (Table 1) all give AN advantages over bulkier, more viscous PC and much bulkier DME.

Acknowledgement

This work was supported, in part, by a grant from NERDDC, Australia.

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