NEW ANIONS AS SUPPORTING ELECTROLYTES FOR RECHARGEABLE LITHIUM BATTERIES

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Summary

Each of the two most commonly used salts in ambient-temperature rechargeable lithium batteries has problems involving safety and long-term stability. For example, solutions of $LiClO_4$ in 1,3-dioxolane are shock sensitive while $LiAsF_6$/ether electrolytes degrade (both thermochemically and electrochemically) with time. Studies have been undertaken on the solubility, conductivity, and stability towards lithium of seven new lithium salts in both tetrahydrofuran (THF) and sulfolane. Of the seven salts, $LiTaF_6$, $Li_2C_2F_4(SO_3)_2$ and $Li_2C_4F_8(SO_3)_2$ provide reasonable conductivities and good stability in sulfolane at 70 °C.

Introduction

The key problem retarding the development of rechargeable lithium batteries is the poor cycleability of the lithium electrode. Although major advances in this technology have been made over the last five years, significant improvements in controlling the lithium/electrolyte reactivity are still required [1]. Solvents such as 2-methyltetrahydrofuran (2-MeTHF), 2-methylfuran (2-MeF), and sulfolane are known to be kinetically stable towards lithium [2]. However, all of these solvents require $LiAsF_6$ as a supporting electrolyte to achieve lithium-electrode cycling efficiencies in excess of 97% [2]. This salt is thermochemically and electrochemically unstable in prototype batteries and therefore greatly limits further progress in rechargeable lithium technology [3, 4].

Other salts, such as LiBr, $LiClO_4$, $LiBF_4$, LiSCN, $LiPF_6$, $LiBR_4$ (R = alkyl) and $LiB(Ar)_4$, fail to perform well for reasons of reactivity with lithium and/or poor conductivity [1]. The $LiClO_4$/1,3-dioxolane electrolyte reported by the EXXON group gives excellent lithium cycleability, but because of its propensity to detonate both on impact and overdischarge, further work with this electrolyte has been abandoned [5].

We have evaluated seven new lithium salts that may be divided into three classes: (i) perfluorinated alkyldisulfonates, (ii) oxocarbons, and (iii) inorganic analogues of $LiAsF_6$. The solubility, conductivity, and stability of these salts towards lithium have been examined in both THF (25 °C) and sulfolane (70 °C and 100 °C).

Experimental

General

Electrolytes were prepared under an argon atmosphere in a dry box (Vacuum-Atmospheres Corporation) equipped with a Model HE-493 Dri-Train. Conductivity measurements were obtained at 1 kHz with a YSI 3400 dip-type conductivity cell on a Gen Rad 1650A impedance bridge. The solubilities of the oxocarbon lithium salts in aprotic organic media were determined by atomic absorption analysis for Li^+ in equilibrated solutions using a Perkin Elmer Model 403 AA spectrophotometer. Elevated temperatures were maintained by either an Omega 4001 thermocontroller (± 1 °C) or by a Thelco Model 27 oven (± 3 °C).

Materials

Tetrahydrofuran (THF) (Burdick and Jackson, UV grade, distilled-in-glass), $LiAsF_6$ (US Steel Agri-Chemicals, electrochemical grade), $LiTaF_6$, and Li_2GeF_6 (Research and Productivity Council, Fredericton, N.B., Canada, supplied in sealed Pyrex ampouls) were used as received. Lithium foil (10 mil) (Foote Mineral Company) was used as received and exposed only to the dry-box atmosphere.

Sulfolane (99.5%) (Fluka) was stirred over activated charcoal at 100 °C, decanted, and then stirred over NaOH pellets overnight at 100 °C prior to vacuum distillation under argon according to the procedure of Foos and Brummer [6]. Sulfolane-based electrolytes were prepared at ambient temperature followed by pre-electrolysis at 70 °C between two lithium electrodes.

Dilithium squarate ($Li_2C_4O_4$) and dilithium rhodizonate ($Li_2C_6O_6$) were prepared from squaric and rhodizonic acids (Aldrich), as described previously [7]. Dilithium croconate ($Li_2C_5O_5$) was supplied by Dr A. Fatiadi (National Bureau of Standards) and was used as received.

Dilithium 1,2-perfluoroethyldisulfonate $\{Li_2C_2F_4(SO_3)_2\}$ and dilithium 1,4-perfluorobutyldisulfonate $\{Li_2C_4F_8(SO_3)_2\}$ were obtained from the 3M Company (Minneapolis, MN) and were dried under vacuum at 160 °C over P_2O_5 prior to use.

Lithium/electrolyte storage tests

Samples of electrolyte and freshly scratched lithium foil were incubated in Teflon-lined screw-cap culture tubes (Corning, C9826) at 70 $\pm$ 3 °C. Visual observations of electrolyte condition were made on a day-to-day basis.

Results and discussion

Oxocarbon salts

Three members of an homologous series of cyclic dianions, known as "oxocarbons" and having the general formula $C_nO_n^{2-}$, were chosen for
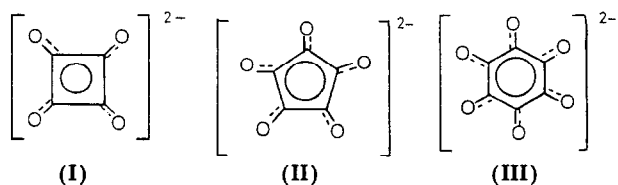
Fig. 1.

evaluation. The infrared and Raman spectra of the sodium and lithium salts of the squarate (I), croconate (II), and rhodizonate (III) (Fig. 1) show that these species are symmetrical and have aromatic properties owing to charge delocalization over the entire π-system of the oxocarbon rings [8]. The pseudo-aromaticity of these compounds suggests a resistance to reduction in aprotic solvents.

The solubilities and conductivities of the dilithium salts of the above three oxocarbon anions are presented in Table 1. In THF at 25 °C, all three salts are from 4 to 6 orders of magnitude less soluble than $LiAsF_6$ under similar conditions, i.e., 1.5 M $LiAsF_6$/THF where $K_{sp} = 1.7 \times 10^{-2}$ (ohm cm)$^{-1}$ at 25 °C [9]. The measured conductivities of these electrolytes are invariant owing to ion-pair formation. In sulfolane at 100 °C, solubilities and conductivities are seen to marginally increase. Accordingly, these materials are not useful as supporting electrolytes for lithium batteries.

TABLE 1

Solubility and conductivity of dilithium oxocarbon salts in THF (25 °C) and sulfolane (S) (100 °C)

Salt	Solvent	Maximum concentration (mol dm^{-3})	Specific conductance (ohm cm)$^{-1}$
$Li_2C_4O_4$ (I)	THF	1.08×10^{-4}	8.3×10^{-7}
	S	2.25×10^{-4}	8.3×10^{-6}
$Li_2C_5O_5$ (II)	THF	2.5×10^{-5}	8.3×10^{-7}
	S	—	6.1×10^{-6}
$Li_2C_6O_6$ (III)	THF	5.4×10^{-6}	8.3×10^{-7}
	S	2.4×10^{-4}	3.1×10^{-6}

Analogues of $LiAsF_6$ and perfluorodisulfonates

Two analogues of $LiAsF_6$, $LiTaF_6$ and Li_2GeF_6, were synthesized by the Research Productivity Council. Kinetic arguments suggest that the TaF_6^- and GeF_6^{2-} ions are both thermally stable and more resistant to reduction than is AsF_6^-. The large TaF_6^- core metal atom parallels the observed kinetic stability of the series $AsF_6^- > PF_6^- > BF_4^-$. Moreover, the GeF_6^{2-} dianion is isoelectronic with AsF_6^-.

TABLE 2

Maximum solubility and conductivity of various lithium salts in THF and sulfolane (S)

Salt	Solvent	Temperature (°C)	Concentration (mol dm^{-3})	Specific conductance (ohm cm)$^{-1}$
LiTaF$_6$	THF	23	1.20	—*
	S	75	0.33	3.8×10^{-3}
Li$_2$GeF$_6$	THF	23	0.000 07	1.6×10^{-6}
	S	75	0.015	7.1×10^{-6}
Li$_2$C$_2$F$_4$(SO$_3$)$_2$	THF	21	0.6 ± 0.1	4.5×10^{-4}
	S	70	0.3 ± 0.1 (sat.)	7.8×10^{-4}
Li$_2$C$_4$F$_8$(SO$_3$)$_2$	THF	21	≈ 0.001 (sat.)	4.3×10^{-6}
	S	70	0.4 ± 0.1	9.7×10^{-4}

*THF polymerized in the presence of LiTaF$_6$.

Table 2 shows that while LiTaF$_6$ is quite soluble in THF, the electrolyte rapidly polymerized, presumably because of the release of TaF$_5$ by the TaF$_6^-$ anion. In sulfolane at 75 °C, LiTaF$_6$ affords a specific conductance equivalent to that of 1.4 M LiAsF$_6$/2-MeTHF at 25 °C [9].

Li$_2$GeF$_6$ was some 200 times more soluble in sulfolane than in THF, but only 4 times more conductive. Again, strong ion-pairing must be in force here. Clearly, spatially small dianions which concentrate the two negative charges into a small volume element will not provide suitably conductive solutions in aprotic organic solvents.

The two perfluoroalkyldisulfonates supplied by the 3M Company gave marginal conductivities in sulfolane at 70 °C but were poorly conductive in THF at room temperature (Table 2). For comparison, 0.8 M monoanionic lithium triflate (LiCF$_3$SO$_3$) gave a conductivity of 9.0×10^{-4} (ohm cm)$^{-1}$ in sulfolane at 30 °C [10].

Because the 1,2-perfluoroethyldisulfonate dianion is simply a dimer of triflate, the poorer solubility (on a mole-for-mole basis) is due to the larger molecular weight of the dianion. More solvent–solvent interactions (dispersion forces) are disrupted by the larger anion with no compensating solute–solvent interactions as a result of CH$_2$ ... CF$_2$ interactions being weaker than CH$_2$ ... CH$_2$ interactions. Conductances are lower on a one-to-one Li$^+$ ion concentration basis of comparison, at least in part, owing to the lower mobility of the heavy anion. Another likely source of lower conductivity arises from solvation of the heavy anion which is itself a contact ion pair. This species is strongly solvated by at least two solvent molecules, whereas the triflate anion is not strongly solvated. The strong solvation of the second Li$^+$ ion on the heavy anion reduces the amount of solvent available to coordinate with the first Li$^+$ ion, thereby depressing dissociation. Finally, the (probable) much higher viscosity of the solution of dianions also lowers the conductivity relative to triflate.

Conclusions

None of the new salts provided adequate conductivity in THF at room temperature and, therefore, would not be expected to provide a sufficiently conductive electrolyte in either 2-MeTHF or 1,3-dioxolane. In sulfolane at elevated temperatures, $LiTaF_6$ is adequately conductive, while $Li_2C_2F_4(SO_3)_2$ and $Li_2C_4F_8(SO_3)_2$ exhibit only marginal conductivities. Stability tests of saturated sulfolane solutions of these three salts at 70 °C in the presence of lithium foil have revealed no visible reactivity over a four-week period.

Acknowledgements

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