SOLVENT EFFECTS ON RECHARGEABLE LITHIUM CELLS

M. UCHIYAMA, S. SLANE, E. PLICHTA and M. SALOMON

US Army, LABCOM, Power Sources Division, Fort Monmouth, NJ 07703-5302 (U.S.A.)

Summary

The behaviour of several solvents in rechargeable lithium cells employing two different structure type cathodes, ns-V_6O_{13} a framework oxide, and TiS_2 a layered material, was compared. Excellent cycling behaviour and high energy were obtained for the Li/ns-V_6O_{13} cell at current densities as high as 5 mA cm^{-2} in the temperature range 25 to −40 °C. Cells utilizing an electrolyte of 2 M $LiAsF_6$ in methyl formate were discharged at a current density of 2 mA cm^{-2} at −40 °C with 37% cell efficiency at an energy density of 255 W h kg^{-1} (based on active material). Use of an $LiAsF_6$/2--MeTHF electrolyte with ns-V_6O_{13} resulted in satisfactory cycle-life, but at significantly reduced capacities than observed with the $LiAsF_6$/MF electrolyte. This is attributed to the lower conductivities of 2-MeTHF solutions.

The results for Li/TiS_2 cells are in direct contrast with those observed for ns-V_6O_{13}. Use of MF solutions with TiS_2 results in extremely low capacities while capacities and cycle life in 2-MeTHF solutions are quite good. These differences are attributed to a combination of factors including solvent co-intercalation, ion solvation, and solvent decomposition.

Introduction

The development of a lithium rechargeable battery for military applications requires the capability to operate over a wide temperature range. Because of this requirement, the selection of a solvent/electrolyte combination is of major importance. In previous work [1], it has been shown that an Li/TiS_2 cell can operate down to −40 °C in $LiAsF_6$ and $LiAlCl_4$ solutions in a preferred binary solvent containing 24 wt.% 4-butyrolactone in 1,2-dimethoxyethane (referred to as the DME/BL mixture in discussions below). Although the TiS_2 cathode is capable of providing high rates for up to 70 cycles (low-rate cycle life is much higher), its energy density drops rapidly at low temperatures. For example, at −40 °C, a discharge efficiency of approximately 12% was obtained [1]; this corresponded to an energy density of only 42 W h kg^{-1} (based on active materials). In pursuing alternative intercalating cathodes for use in a lithium rechargeable cell, selection of non-stoichiometric V_6O_{13} was made on the basis of previous studies that

demonstrated high reversibility, high rate capabilities, and high energy densities [2 - 6].

One of the problems to be addressed when using very highly energetic cathodes such as ns-V_6O_{13} is the stability of the solvent at high cathodic potentials. Ebner *et al.* [6] have shown that methylformate (MF) exhibits excellent stability towards ns-V_6O_{13}, and MF solutions have the advantage of being highly conductive [7]. The present study reports new results for the Li/ns-V_6O_{13} cell in a number of solvents, including MF, 2-methyltetrahydrofuran (2-MeTHF), binary mixtures of 1,2-dimethoxyethane (DME) with 4-butyrolactone (BL), and dimethylsulfite (DMSI). Studies have been carried out over the temperature range -40 °C to 25 °C, and the findings are compared with previously published data.

Experimental

Chemicals

1,2-Dimethoxyethane (DME) (Burdick and Jackson "Distilled in Glass" grade) and nitromethane (NM) (Aldrich Gold Label) were both dried with 4A molecular sieves prior to use. 4-Butyrolactone (BL) (Aldrich Gold Label) was magnetically stirred with a mixture of 4A and 5A molecular sieves for 10 h under a dynamic argon atmosphere, and then fractionated under vacuum. 2-Methyltetrahydrofuran (2-MeTHF) (Aldrich) and methylformate (MF) (Alfa Chemicals, 99+%) were similarly pre-treated and fractionated under an argon atmosphere. Dimethylsulfite (Aldrich Chemicals, 99% purity) was dried with 4A molecular sieves for 24 h and then fractionated twice under reduced pressure. In each fractionation, the middle fraction was collected at 65 °C. All solvents were stored in an argon filled dry box (Vacuum Atmospheres).

$LiAsF_6$ (USS Agri Chemicals "Electrochemical Grade") was dried under vacuum at 60 °C for 24 h and then stored in the above dry box. Ammonium metavanadate (NH_4VO_3) was obtained from Alfa Products and used as received.

Conductivity measurements

Electrolyte solutions were prepared by weight in the dry box, and densities of each stock solution were measured with a digital density meter. Aliquots of a given stock solution were used to prepare additional solutions by successive weight dilution. Jones-type conductivity cells were used ($k = 1.0$ cm^{-1}) and were calibrated with aqueous KCl solutions. Conductivities were measured at 1 kHz with a Wayne Kerr B905 precision bridge. All conductivity measurements were carried out in the laboratory in a water bath thermostatted at 298.15 ± 0.02 K.

Preparation of non-stoichiometric V_6O_{13}

Non-stoichiometric V_6O_{13} was prepared by the thermal decomposition of NH_4VO_3 at 450 °C in a Lindberg Model tube furnace under a flow of

argon. In a typical preparation, 12 g of NH_4VO_3 were placed in a pre-dried quartz tube (25 mm i.d.) under an argon flow rate of 0.01 min^{-1}. The product was a blue–black powder and its stoichiometry was determined gravimetrically. An O/V ratio of 2.19 was obtained. The X-ray powder diffraction (XRD) pattern of the product was similar to that reported for stoichiometric V_6O_{13} [8].

The sensitivity of ns-V_6O_{13} to water was tested by stirring a 100 mg sample of ns-V_6O_{13} in 20 ml H_2O at 25 °C for 0.5 h. The solid was then filtered and dried under vacuum at 60 °C for 24 h. The XRD pattern remained unchanged.

Laboratory cells

A cathode mix of 70 wt.% ns-V_6O_{13}, 20 wt.% Shawinigan acetylene black, and 10 wt.% Teflon was prepared using an aqueous Teflon emulsion. The cathodes were sintered under vacuum at 280 °C and then compacted under a pressure of 1400 psi.

The laboratory test cells consisted of a wick configuration utilizing flag electrodes in a pressure reaction vessel. A lithium anode on each side of the cathode was separated by a porous fibre separator (wick). The electrodes were sealed in Celgard 2400 polypropylene separator material. Nickel screen (Annealed Exmet Ni 7-3/0) was used as the current collector.

The test cells were cycled between 3.0 V and 1.9 V in Tenney Environmental chambers at constant currents using ECO Instrument Model 545 galvanostat-electrometers. Note, all potentials are reported *versus* a lithium reference electrode. All cells were charged at 25 °C using a current density of 0.5 mA cm^{-2}. The efficiencies of Li/ns-V_6O_{13} cells reported below are based on an Li/V ratio of one, *i.e.*, for 100% efficiency, one mole of ns-V_6O_{13} will reversibly intercalate six moles of lithium.

Results

The XRD patterns for ns-V_6O_{13} and water-treated ns-V_6O_{13} are virtually identical. Therefore, it is possible to prepare cathodes using an aqueous Teflon suspension as the binder. Such prepared cathodes are highly flexible and possess a porosity ranging between 57% and 62%. The shape of the constant-current discharge/charge curves of Li/ns-V_6O_{13} cells prepared from these cathodes is identical with that observed in previous studies [2 - 6].

The conductivities of 1 and 2 M $LiAsF_6$ solutions in binary mixtures of MF with BL and with NM are slightly higher than those in pure MF at compositions less than 15 wt.% additive [9]. For example, in a 10 wt.% NM in MF mixture, the electrolytic conductivity of a 2 M $LiAsF_6$ solution is 0.047 S cm^{-1} at 25 °C, as compared with 0.043 S cm^{-1} at 25 °C for pure MF [7]. In studies of the effect of additives, we used 2 M $LiAsF_6$ in mixtures containing 17 wt.% NM and 19 wt.% BL in MF. For conductivities of $LiAsF_6$ in DME/DMSI mixtures, a conductivity maximum was observed for

compositions containing 76 - 78 wt.% DMSI. For example, in a mixture containing 76.7 wt.% DMSI, the electrolytic conductivity of a 0.92 M LiAsF$_6$ solution is 0.018 S cm^{-1} at 25 °C, 0.0036 S cm^{-1} at −42 °C, and 0.0027 S cm^{-1} at −51 °C.

The effect of the solvent on the cycling behaviour of the Li/ns-V$_6$O$_{13}$ cell is shown in Fig. 1. The cells were discharged/charged at 1.0/0.5 mA cm^{-2} between 3.0 V and 1.9 V. Significant degradation was observed in both mixed solvents, and cycling was terminated after 7 - 10 cycles. Further comparisons of the cycling efficiency of the Li/ns-V$_6$O$_{13}$ cell in different solvents are made in Fig. 2, i.e., for 2.0 M LiAsF$_6$ in MF, 1.3 M LiAsF$_6$ in 2-MeTHF, and 1.3 M LiAsF$_6$ in a DME/BL mixture containing 24 wt.% BL
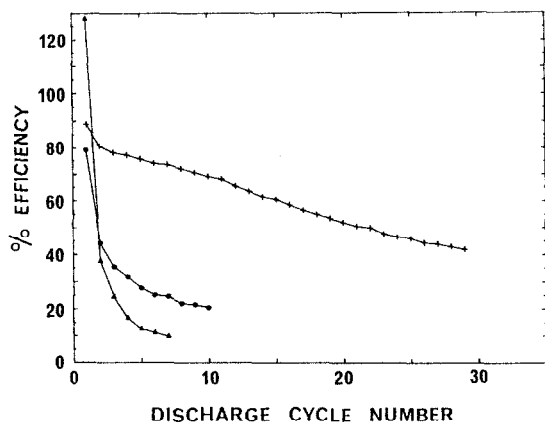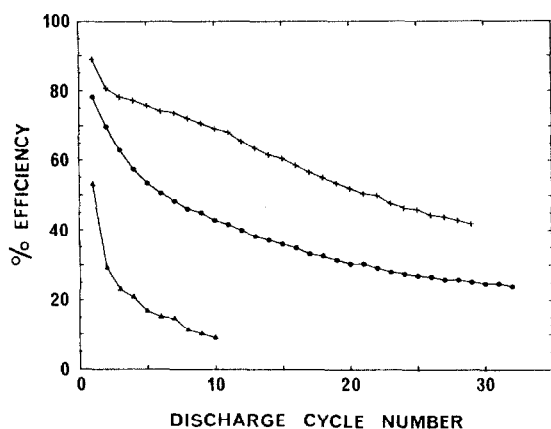

Fig. 1. Cycling efficiency at 25 °C of Li/ns-V$_6$O$_{13}$ cells in various solvents. Cycling between 3.0 and 1.9 V (vs. Li) at 1.0 mA cm^{-2} discharge and 0.5 mA cm^{-2} charge. +, Li/ns-V$_6$O$_{13}$ in 2.0 M LiAsF$_6$ in MF; ●, Li/ns-V$_6$O$_{13}$ in 1.9 M LiAsF$_6$ in BL/MF; ▲, Li/ns-V$_6$O$_{13}$ in 2.2 M LiAsF$_6$ in NM/MF.

Fig. 2. Cycling efficiency at 25 °C of Li/ns-V$_6$O$_{13}$ cells in various solvents. Cycling between 3.0 and 1.9 V (vs. Li) at 1.0 mA cm^{-2} discharge and 0.5 mA cm^{-2} charge. +, Li/ns-V$_6$O$_{13}$ in 2.0 M LiAsF$_6$ in MF; ●, Li/ns-V$_6$O$_{13}$ in 1.3 M LiAsF$_6$ in 2-MeTHF; ▲, Li/ns-V$_6$O$_{13}$ in 1.3 M LiAsF$_6$ in BL/DME.

[1]. Although all the cells exhibited degradation upon cycling, that in the DME/BL mixture was particularly rapid whereas that in MF was the least degraded. The results for the Li/ns-V_6O_{13} cell in mixtures of DME and DMSI are not shown because the cell degraded rapidly after only one cycle. In 1 M LiAsF$_6$ in a DME/DMSI mixture containing 78 wt.% DMSI, the efficiency was 49% on the first cycle, and significant solvent reduction at 2.1 V was observed.

The effect of discharge rate on cycle behaviour for the Li/ns-V_6O_{13} cell is given in Fig. 3 which also includes excursions to −10 °C and −40 °C. Very similar behaviour is observed at 1 and 2 mA cm^{-2}, whereas slightly lower capacities were seen at the highest rate. The capacities at −10 °C and −40 °C were virtually independent of the discharge rate. The low-temperature behaviour of Li/LiAsF$_6$ in MF/ns-V_6O_{13} cells was studied in more depth using constant-potential cycling at 25 °C, −10 °C and −40 °C. The discharge/ charge cycles at 25 °C and −10 °C are compared in Fig. 4. Integrated capacities in the three potential regions 3.00 → 2.65 V, 2.65 → 2.30 V, and 2.30 → 1.90 V exhibit 8%, 3%, and 47% loss, respectively, at −10 °C as compared with the capacities for the same potential regions at 25 °C. At −40 °C the capacity losses are, respectively, 24%, 11% and 82% of that observed at 25 °C in the same potential regions.

Figure 5 compares the cycling behaviour for the Li/TiS$_2$ cell with 0.83 M LiAlCl$_4$ in DME/BL [1], 1.7 M LiAsF$_6$ in 2-MeTHF, and 2.0 M LiAsF$_6$ in MF [6, 10]. Cells utilizing the 2-MeTHF and DME/BL electrolytes maintained good capacities on extended cycling, whereas the cell in MF exhibited a dramatic capacity loss after 5 cycles; continued cycling showed little change in the experimental capacity.
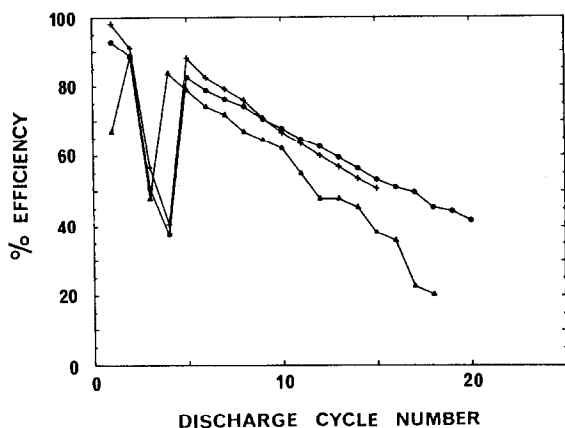

Fig. 3. Cycling efficiency of Li/ns-V_6O_{13} in 2.1 M LiAsF$_6$ in MF at various discharge current densities. For each current density, the third discharge was performed at −10 °C. The fourth discharge for the current densities of 1 and 2 mA cm^{-2} was at −40 °C. Discharge current density: +, 1.0; ●, 2.0; ▲, 5.0 mA cm^{-2}.
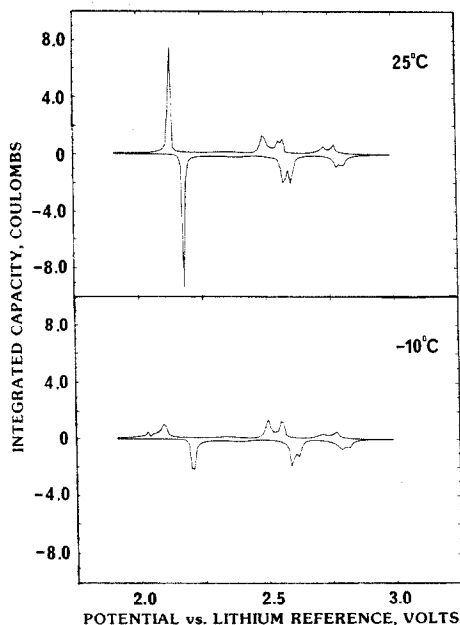
Fig. 4. Second and third constant-potential cycles of Li/ns-V_6O_{13} cell in 1.9 M $LiAsF_6$ in MF at 25 °C and −10 °C, respectively. Cathode surface area: 0.982 cm^2. Potential step of 10 mV applied to a cut-off current density of 0.1 mA cm^{-2}.
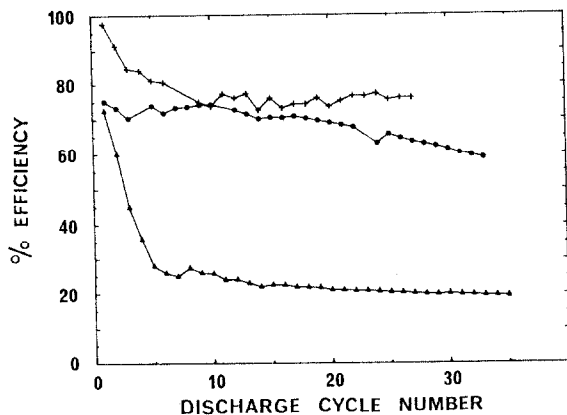

Fig. 5. Cycling efficiency at 25 °C of Li/TiS_2 cell in various solvents. +, 84 wt.% TiS_2/ 8 wt.% Shawinigan acetylene black/8 wt.% Teflon 1.7 M $LiAsF_6$ in 2-MeTHF. Discharge/ charge current densities = 1.0/0.5 mA cm^{-2} [9]; ●, 80 wt.% TiS_2/10 wt.% Shawinigan acetylene black/10 wt.% polypropylene 0.83 M $LiAlCl_4$ 24 wt.% BL/DME. Discharge/ charge current densities = 2.0/0.5 mA cm^{-2}; ▲, 85 wt.% TiS_2/10 wt.% graphite/5 wt.% EPDM in 2 M $LiAsF_6$ + 0.4 M $LiBF_4$ in MF. Discharge/charge current densities = 1.0/ 1.0 mA cm^{-2} [6].

Discussion

The results obtained in this work clearly demonstrate that lithium cells with ns-V_6O_{13} cathodes in $LiAsF_6$/MF are superior in limited cycling to any

cell using TiS_2 cathodes. Excellent behaviour is observed for the ns-V_6O_{13} cell down to -40 °C and at current densities up to 5 mA cm^{-2}.

Significantly, capacities at low temperature were virtually independent of discharge rate. Constant-potential cycling has shown that the most dramatic loss in capacity at low temperatures was in the $2.30 \rightarrow 1.90$ V region. This can be explained by the substantial increase in electronic resistivity of ns-V_6O_{13} at high lithium contents (Li/V $\geqslant 0.6$) [4] and at lower temperatures [11] resulting in high ohmic overpotential. The cut-off voltage limit of 1.9 V is reached before the cathode can be fully lithiated.

The high vapour pressure of methylformate solutions is undesirable for higher temperature applications, and to avoid this problem binary mixtures of MF with NM and BL have been investigated. Although a slight increase in conductivity is observed at low wt.% of these additives (see Fig. 1), ns-V_6O_{13} cells utilizing these binary mixtures exhibit a rapid decline in capacity upon cycling.

The results for Li/TiS_2 cells are in direct contrast to those observed for Li/ns-V_6O_{13}. Use of MF solutions with TiS_2 results in extremely low capacities, whereas capacities and cycle life in 2-MeTHF and DME/BL solutions are quite good. With ns-V_6O_{13} cells, lower capacities are observed for 2-MeTHF as compared with MF solutions, and this is attributed to the low conductivities of 2-MeTHF solutions.

It is apparent that for Li/$LiAsF_6$–MF/TiS_2 cells, the solvent co-intercalates with the cation, probably followed by solvent reaction in the layered structure of TiS_2. Reasons for the superiority of 2-MeTHF and DME/BL solutions with TiS_2 appear to be much more complex. Clearly, factors involving solvent co-intercalation, ion solvation, and solvent decomposition are important. Although more data are necessary, this difference may simply be the result of considerably lower reactivities of 2-MeTHF and DME/BL mixtures in the TiS_2 lattice, coupled with stronger lithium-ion solvation in etheral solvents [12].

Unlike TiS_2, in which intercalation takes place between layers weakly bonded by van der Waals forces, ns-V_6O_{13} is a channelled structure and much more specific towards lithium insertion [4, 5]. Thus, solvent molecules do not co-intercalate with lithium. The capacity loss with cycling of ns-V_6O_{13} cathodes is attributed to lattice expansion upon intercalation resulting in mechanical separation of active material from the current collector [4, 5], and the oxidation of solvents such as DMSI, NM, BL and 2-MeTHF at the high cathode potentials characteristic of ns-V_6O_{13}.

Conclusion

This work demonstrates the excellent cycling behaviour, high energy, and high rate capabilities over a wide temperature range of the Li/ns-V_6O_{13} cell. In addition, practical ns-V_6O_{13} cathodes can be fabricated with aqueous Teflon suspensions. At this time, a 2 M $LiAsF_6$ solution in methylformate is

the electrolyte of choice. Using this electrolyte, Li/ns-V_6O_{13} cells could be discharged at rates up to 2 mA cm^{-2} down to -40 °C with 37% efficiency at an energy density of 255 W h kg^{-1}.

Acknowledgements

References

1 E. J. Plichta and M. Salomon, *J. Power Sources, 13* (1984) 319.
2 D. W. Murphy, P. A. Christian, F. J. DiSalvo, J. N. Carides and J. V. Waszczak, *J. Electrochem. Soc., 128* (1981) 2053.
3 K. M. Abraham, J. L. Goldman and M. D. Dempsey, *J. Electrochem. Soc., 128* (1981) 2493.
4 K. West, B. Zachau-Christiansen and T. Jacobsen, *Electrochim. Acta, 38* (1983) 1829.
5 K. West, B. Zachau-Christiansen, T. Jacobsen and S. Atlung, *J. Power Sources, 14* (1985) 235.
6 W. B. Ebner, H. W. Lin and P. N. Lensi, *ERADCOM 1st Quarterly Report, No. DELET-TR-84-0412-1* (see also subsequent reports, Nos. 2 - 6).
7 H. V. Venkatasetty, *J. Electrochem. Soc., 122* (1975) 245.
8 K.-A. Wilhelmi, K. Walterson and L. Kihlborg, *Acta Chem. Scand., 25* (1971) 2675.
9 M. Uchiyama, S. Slane, E. J. Plichta and M. Salomon, in L. Pearce (ed.), *Power Sources 11,* in press.
10 E. J. Plichta and M. Salomon, unpublished data obtained using a cell provided by EIC, Inc. and electrolyte prepared by the authors.
11 M. Uchiyama, S. Slane and M. Salomon, unpublished data.
12 M. Salomon, in P. S. Glaeser (ed.), *The Role of Data in Scientific Progress, Proc. 9th Int. CODATA Conf.*, Elsevier, North-Holland, Amsterdam, 1985.