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General paper

SOLVENT MATERIALS FOR USE IN ELECTROLYTE SOLUTIONS OF RECHARGEABLE CELLS WITH LITHIUM METAL ANODES

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Abstract: A rechargeable cell with a lithium metal anode (lithium metal cell) is attractive because theoretically it has a high energy density. The problems with lithium metal cells are their short cycle life and poor safety resulting from their low cycling efficiency and the high chemical reactivity of lithium. One of the most important factors is the selection of the electrolyte materials. In this paper, we examine the influence of the composition of ternary mixed solvent electrolytes comprising ethylene carbonate (EC), propylene carbonate (PC) and 2-methyltetrahydrofuran (2MeTHF) on the properties of AA-size Li/a-V₂O₅-P₂O₅ cells. The goals are to improve the cycle life of the cell while ensuring its safety and controlling its cost. The cell performance examined here includes cell capacity and charge-discharge cycle life. We also carried out a heating abuse test at 130 °C on the Li/a-V₂O₅-P₂O₅ cells. The best electrolyte composition was found to be 1.15M LiAsF₆-EC/PC/2MeTHF (15:70:15) from our overall results on cycle life, capacity, safety and cost.

Key Words: Lithium, Rechargeable cell, Electrolyte solution, Amorphous vanadium oxide

1. INTRODUCTION

Demands for an increase in the energy density of rechargeable cells have been increasing because of various new applications, including electric vehicles, load leveling and various types of portable equipment. A rechargeable cell with a lithium metal anode (lithium metal cell) is attractive because theoretically it has a high energy density. However, cylindrical type lithium metal cells are not commercially available. The problems with lithium metal cells are their short cycle life and poor safety resulting from their low cycling efficiency and the high chemical reactivity of lithium. One of the most important factors related to these problems is the selection of the electrolyte solution. Ultimately, the composition, including the solvent mixing ratio and the salt concentration, should be optimized and the electrolyte materials carefully chosen, when determining a suitable electrolyte for practical applications.

In a previous study [1], we reported the influence of the mixing ratio of ethylene carbonate (EC) and propylene carbonate (PC) solvents, in EC/PC binary mixed solvent systems incorporating LiAsF₆ as the solute, on the cycle life and safety of AA cells consisting of an amorphous (a-) V₂O₅-P₂O₅ cathode and a lithium (Li) metal anode [2]. We found the maximum cycle life was obtained with an EC content of 10-30 vol.% with a relatively high capacity. This result is believed to relate to the interaction between EC and Li_xV₂O₅ [1,3]. The influence of the addition of a small amount of 2-methyl-tetrahydrofuran (2MeTHF) to an EC/PC binary mixed system on AA Li/a- V₂O₅-P₂O₅ cell properties has also

been briefly examined [1]. Based on such considerations as safety, cost and ease of handling in a manufacturing

plant, a lower 2MeTHF content would be better. This is because 2MeTHF has a low flash point of -11°C, a low boiling point of 79°C, it is easily oxidized leading to the formation of dangerous peroxide, it is hygroscopic and its cost is about five times that of EC or PC [4]. In addition, an investigation of the thermal stability of organic electrolytes by accelerating rate calorimetry (ARC) [5] indicated that, in terms of safety, the preferable 2MeTHF content of an organic electrolyte system is less than 15 vol.%.

In this report, we examine the influence of the composition of EC/PC/2MeTHF ternary mixed solvent electrolyte on the properties of AA-size Li/a-V₂O₅-P₂O₅ cells with a view to improving the cycle life of the cell while ensuring its safety and controlling its cost. In this work, the 2MeTHF content is fixed at 15 vol.% based on the results of previous studies related to safety and cost [1,5]. The material cost of EC/PC/2MeTHF (15 vol.% 2MeTHF) is about twice that of the EC/PC binary mixed system. We vary the electrolyte composition by changing the mixing ratio of the EC and PC solvents (EC:PC is 5:85-42.5:42.5) and the LiAsF₆ concentration (0.75-1.5 mol 1⁻¹). The cell properties include capacity and cycle life. We also performed a heating abuse test.

2. EXPERIMENTAL

2.1. Electrolytes

Our electrolyte solutions were prepared as described in previous papers [6,7]. The water content was less than 20

ppm. Hereafter, "1M LiAsF6-EC/PC(1:1)" will be used to indicate an electrolyte solution of mixed EC and PC solvents (mixing volume ratio=1:1) dissolved in 1M (M:mol/I) LiAsF6. Electrolyte conductivity was measured at 1kHz with an LCR bridge (Gen Rad Co., model 1658).

2.2. Fabrication of Li/a-V2O5-P2O5 Cell

The cell used here is an AA-size laboratory-type cell and its structure is very similar to that of the Li/MoS₂ cell fabricated by Moli Energy Ltd. [8,9]. This cell has a pressure vent in the bottom surface of its cell casing and is composed of a spirally wound Li metal anode sheet, a polyethylene separator, a printed cathode sheet of a-V2O5-P2O5 (~150µm), polymer binder and conductive carbon. a-V2O5-P2O5 (95 mole% V2O5) was prepared by melting reagent-grade raw oxides in platinum crucibles for an hour at 750 °C, followed by quenching on a watercooled iron block [10]. The cell had a capacity of about 600mAh. Charge-discharge cycle tests were carried out on the AA cells with a charge cut-off voltage of 3.3V and a discharge cut-off of 1.8V [2]. The cell operation temperature was 21°C. The cycle life of the AA-cells was evaluated by the figure of merit (FOM) defined in Eq.(1), and by setting the end of cycle life at the cycle number where the discharge capacity fell to 50% of the maximum capacity. FOM is related to cycling efficiency (Eff,%) as shown in Eq.(2). The definition of FOM is the cycling number of one atom of lithium until it becomes electrochemically inactive. Lithium anode is consumed during cycling. Generally, FOM is determined by cycling efficiency of lithium.

$$FOM=100/(100-Eff)$$
 (2)

2.3. Abuse Tests

Heating tests were carried out by placing the cells in a pre-heated incubator [11,12].

3. RESULTS AND DISCUSSION

3.1. Physical Properties of Solvents

Table 1 shows the physical properties of EC, PC and 2MeTHF, respectively [6,13,14]. EC and PC are highly dielectric esters which are effective for the ionic dissociation of the electrolyte salt and these solvents have high flash point (Fp) which exceed 100 °C. EC and PC have many practical advantages. These include ease of handling because of their high chemical stability, a high boiling point and a high Fp, low toxicity and low cost. By contrast, 2MeTHF is a low viscosity ether which is effective in terms of ion migration. It has a low boiling point of 79°C and a low Fp of -11°C, that is considerably below room temperature. In addition, 2MeTHF has a stronger solvation power for Li⁺ ions than EC and PC, as predicted from the donor numbers of these solvents [14].

From a practical point of view, it is clear that the Fp should be as high as possible. Based on considerations including safety, cost and ease of handling in a manufacturing plant, it would be preferable to have a lower 2MeTHF.

3.2. Basic Composition of Electrolyte System

EC/PC/2MeTHF(15:70:15) was briefly tested as a practical AA cell electrolyte in previous work [1]. This electrolyte composition was chosen for the following three reasons. First, an AA Li/a-V2O5 -P2O5 cell with an EC/PC binary mixed solvent electrolyte exhibited higher cycleability with an EC/PC mixing ratio range of 1:9-3:7, i.e., when the EC content is 10 to 30% in EC/PC [1]. Second, the best cycleability for a Li/a-V2O5 -P2O5 coin cell containing EC/2MeTHF binary mixed solvent electrolytes is obtained with an EC/2MeTHF mixing ratio of 1:1 [15]. This high cycleability of the coin cell is resulted from the high cycling efficiency of lithium anode by the formation of the suitable surface film to make lithium cycle better. This film is considered to consist of lithium carbonate, lithium alkylcarbonate and polymer compounds having (-O-As-O)n, resulted from

Table 1. Physical Properties of EC, PC and 2MeTHF.

Solvent	ε(25°C)	η(25℃)	<i>mp</i> (℃)	<i>bp</i> (℃)	<i>Fp</i> (℃)	DN
EC	95.3	2.53 ^{a)}	36.4	238	160	16.4
PC	64.4	2.54,	-49	241	132	15.1
2MeTHF	6.2	0.46	-75	79	-11	18

 ε :dielectric constant, η : viscosity, *mp*:melting point, *bp*:boiling point, *Fp*:flash point, *DN*:donor number, a) EC/PC=1:1.



Fig.1. Relation between κ , temperature and EC content in mixed solvents.

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the reactions of lithium with EC, 2MeTHF and LiAsF6 [15]. Third, we took the Fp and the cost of the materials into consideration. When the 2MeTHF content is 15%, the cost is about 1.5 times that of EC/PC [4] and the Fp of the EC/PC/2MeTHF mixed solvents dissolved Li salt could probably be higher than room temperature. Therefore, EC/PC/2MeTHF (15:70:15) is chosen here. In this electrolyte, the ratio of EC/PC is 15:70 (= 18:82) (the EC content is 18% when the total amount of EC/PC is assumed to be 100%) and the EC/2MeTHF ratio is 50:50.

3.3. EC/PC Mixing Ratio in EC/PC/2MeTHF First, we examine the influence of the mixing ratio of

EC and PC in 1M LiAsF₆-EC/PC/2MeTHF ternary mixed solvent systems on the cell properties of AA Li/a-V₂O₅-P₂O₅ cells. In this investigation, the 2MeTHF content is fixed at 15 vol.% as already mentioned above. That is, the total amount of EC/PC in the ternary mixed solvents is 85 vol.% and four different EC/PC mixing ratios (5:80, 15:70, 30:55 and 42.5:42.5) are examined. These EC content values correspond to 6, 18, 35 and 50 vol.%, respectively, when the total amount of EC and PC is assumed to be 100.

Figure 1 shows the relationship between the electrolyte conductivity (κ) and the EC/PC content. At 25°C, the conductivity tends to increase gradually with an increase in EC content and to saturate around 30 vol.% EC. This saturated conductivity is 6.2 mS cm⁻¹ and is just a little higher than the borderline value of 4 mS cm⁻¹ required for practical applications [16]. This low conductivity results from the high viscosity of EC/PC mixed with only 15 vol.% 2MeTHF which is a low viscosity solvent. The viscosity of EC/PC/2MeTHF (15:70:15) measured here is 1.98 cP at 25 °C which is 82.5% of that for EC/PC. When a lithium salt with a large anion such as LiAsF6 is used, solvent viscosity has a greater effect on the improvement in electrolyte conductivity than the dielectric constant. This is because this type of lithium salt has intrinsic ionic dissociation power although the ion migration speed is low [7]. The solvent viscosity must be less than 1 cP to realize a conductivity exceeding 10 mS cm⁻¹ at 25 °C based on our conductivity data for various electrolyte systems [7]. As the temperature is reduced, the EC content exhibiting the maximum conductivity tends to decrease. This is due to the higher activation energy obtained from the Arrhenius plot (log (kT) vs the T plot, where T = absolute temperature ([17]), caused by the higher melting point of EC [75]. However, as shown in Fig.1, in the -10 to 60 °C temperature range, the variation in conductivity caused by a change in EC content is very small and may be practically negligible.

Figure 2 shows an example of the relationship between the discharge capacity and cycle number for an AA Li/a- $V_2O_5-P_2O_5$ cell containing 1M LiAsF₆ -EC/PC/2MeTHF (15:70:15) with discharge and charge currents of 0.6 A and 0.1 A, respectively, cycled between 1.8 and 3.3V.

Figure 3 shows the relationship between the FOM and the discharge capacity of the AA Li/a-V₂O₅-P₂O₅ cell, and the EC content of EC/PC/2MeTHF. The AA cell capacity tends to reach maximum at an EC content of 15 vol.%. However, the difference in the cell capacities is less than 8% in the EC content range of 5 to 42.5



Fig.2. Relation between discharge capacity and cycle number of an AA Li/a-V₂O₅-P₂O₅ cell cycled between 1.8V and 3.3V with discharge and charge currents of 0.6A and 0.1A, respectively.



Fig.3. Relation between the FOM, and discharge capacity, of an AA Li/a-V₂O₅-P₂O₅ cell and the EC content in mixed solvents, with discharge and charge currents of 0.6A and 0.1A, respectively, and a discharge cut-off voltage of 1.8V.

vol.% in EC/PC/2MeTHF. The EC/PC mixing ratio had no practical influence on capacity and this was because changes in the ratio made little difference to electrolyte conductivity. The maximum FOM of the AA cell is obtained at an EC/PC mixing ratio of 15:70 where the EC content is 18 % when the total EC/PC amount is assumed to be 100. This result agrees with that of the previous study [3] which reported that EC/PC binary mixed systems with small amounts of EC (10-30%) exhibit the best FOM for AA Li/a-V2O5-P2O5 cells.

A heating test is a fundamental abuse test and is very effective for evaluating the safety of rechargeable lithium metal cells [11,12]. An appropriate heating temperature is selected above the melting point of the separator, as this may lead to an internal short between the anode and cathode. We adopted a temperature of 130°C in this work because our cell contains a polyethylene separator whose melting point is 125°C. Our heating test results at 130 °C for AA cells cycled using EC/PC/2MeTHF ternary mixed solvent electrolytes with different EC/PC mixing ratios indicate that the pressure vents of the cells remained closed and that the maximum cell skin temperature was between 135 and 145°C. The cells were precycled before the heating tests at discharge and charge currents of 0.6A and 0.1A, respectively, between 3.3V and 1.8V or between 3.5V and 1.8V to the end of cycle. The heating test results we obtained were substantially the same for all the AA cells we examined. By contrast, when 130°C heating tests were carried out on AA Li/a-V2O5-P2O5 those with electrolytes containing 2MeTHF cells, exhibited higher a maximum temperature than those with EC/PC binary mixed solvent electrolytes, as shown in Fig. 4. This larger heat output of electrolytes containing 2MeTHF resulted from an exothermic reaction between LiAsF6 and 2MeTHF [5], i.e., the decomposition of the organic electrolyte, as well as that between lithium and electrolyte [16]. These results indicate that, in terms of safety, it is better to have a low 2MeTHF content.

Therefore, based on the overall results for cycle life, capacity and safety tests, the best solvent mixing composition for EC/PC/2MeTHF is 15:70:15 as regards the electrolytes examined here.

3.4. Lithium Salt Concentration

We examined the influence of LiAsF₆ concentration on the FOM, capacity and safety of the AA cells. We used four different LiAsF₆ concentrations (0.75, 1.00, 1.15 and 1.5M) in EC/PC/2MeTHF (15:70:15) in this investigation.

Figure 5 shows the relationship between electrolyte conductivity, temperature and LiAsF6 concentration. As the temperature decreases, the LiAsF6 concentration exhibiting the maximum conductivity tends to decrease. For example, the conductivity exhibited its maximum value for 1.15M of LiAsF6 at 60°C, for 1.00M of LiAsF6 at 20°C and for 0.75M of LiAsF6 at -10°C. This is because of the increase in the degree of ionic

association of the lithium salt based on the increase in the viscosity with a decrease in temperature [15].

Figure 6 shows the relationship between the FOM, or the discharge capacity of an AA Li/a-V₂O₅-P₂O₅ cell, and the LiAsF₆ concentration. The cells are cycled with a 0.6 A discharge and a 0.1 A charge between 1.8 and 3.3V at 21°C. The capacity reached maximum at around 1.15M of LiAsF₆ and 1.5M of LiAsF₆ exhibited the lowest



Fig.4. Results of heating tests at 130°C for AA Li/a-V₂O₅-P₂O₅ cells cycled 80 times at discharge and charge currents of 0.6A and 0.1A, respectively between 1.8 and 3.3V, cell temperature 1: 1M LiAsF₆-EC/PC/2MeTHF (15:70:15), cell t emperature 2 : 1M LiAsF₆-EC/PC (50:50).



Fig.5. Relation among κ , temperature and LiAsF₆ concentration.

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value. This result is closely related to electrolyte conductivity. The FOM increased with an increase in $LiAsF_6$ concentration.

Figure 7 shows the relationship between the FOM, or the discharge capacity of an AA Li/a-V₂O₅-P₂O₅ cell, and the LiAsF₆ concentration. The cells are cycled with a 0.04 A discharge and a 0.08 A charge between 1.5 and 3.3V at -10°C. With a 0.04 A discharge at -10°C, the capacity was similar for cells with different LiAsF₆ concentrations except for 1.5M LiAsF₆, which exhibited the lowest capacity due to the low electrolyte conductivity. The FOM increased with an increase in LiAsF₆ concentration.

Generally, with a decrease in the depth of discharge, the FOM of both the anode and cathode tend to increase [10,19]. One reason why 1.5M LiAsF6 shows a larger FOM than the others is the shallow discharge depth resulting from the low discharge capacity. Another possible reason for the improvement in FOM with an increase in LiAsF6 concentration may be based on the formation of a suitable film on the Li surface which enhances the Li cycling [16]. This film formation reaction involves the consumption of LiAsF6 during each cycle [16]. In addition, electrolyte depletion is reported as the reason for the end of cycle life of lithium metal cells [19]. This means that as the cycle number increases, the amount of LiAsF6 decreases.

Heating tests were carried out at 130°C for AA Li/V₂O₅-P₂O₅ cells cycled at a high rate discharge of 0.6 A using electrolytes with different LiAsF₆ concentrations. None of the cells showed any dangerous venting. The maximum cell temperature in the heating tests was between 133 and 138°C for the cells with 0.75-1.5 M LiAsF₆ concentration and no severe internal heat output was observed.

If the FOM is the only concern, 1.5M LiAsF6 is the most suitable electrolyte concentration. However, 1.15M LiAsF6 is more appropriate in terms of overall performance including cycleability, capacity (including low temperature behavior), safety and cost from a practical point of view. This is because LiAsF6 is the most expensive of the electrolyte materials.

4. CONCLUSION

We examined the influence of the composition of EC/PC/2MeTHF (2MeTHF:15 vol.%) ternary mixed solvent electrolyte on the charge-discharge properties of AA Li/a-V2O5-P2O5 cells. We also performed a heating test as a fundamental abuse test on the cells. The results revealed the following: 1) With regard to the appropriate EC/PC mixing ratio, EC/PC (15:70) showed the highest capacity and the longest cycle life. 2) With regard to LiAsF6 concentration, 1.15M is the most suitable based on the overall cycle life and capacity including low temperature behavior. Summarizing the cell performance as well as the cost and the safety test results

obtained in this work, we believe the best electrolyte composition for an AA Li/a-V $_2O_5$ -P $_2O_5$ cell among those examined here is 1.15M LiAsF $_6$ -EC/PC/2MeTHF (15:70:15).

LD50 of LiAsF6 is 926mg/kg and is not poisonous [16]. However, various compounds induced by the decomposition of LiAsF6, such as AsF3 and arsenious acid, are toxic. Although the toxicity of these compounds are similar to those obtained from LiPF6 used for commercial lithium ion cells, the use of LiAsF6 for mass production cells should be carefully considered.



Fig.6. Relation among the FOM, capacity of AA Li/a-V2O5-P2O5 cells and LiAsF6 concentration, with a 0.6 A discharge and 0.1 A charge between 1.8 and 3.3V.



Fig.7. Relationship between the FOM, capacity of AA $Li/a-V_2O_5-P_2O_5$ cells and $LiAsF_6$ concentration with a 0.04 A discharge and 0.08 A charge between 1.5 and 3.3V.

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