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Effect of purification of 2-methyltetrahydrofuran/ethylene carbonate mixed solvent electrolytes on cyclability of lithium metal anodes for rechargeable cells

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Abstract

The effects of the purification of $LiAsF_6$–2-methyl tetrahydrofuran (2MeTHF)/ethylene carbonate (EC) mixed solvent organic electrolytes on the charge–discharge cyclability of lithium metal anodes has been investigated by using an accelerated method for evaluating lithium cycling efficiency. This method involves cycle tests on coin cells with an amorphous V_2O_5–P_2O_5 (95:5 molar ratio) cathode and an anode containing a small amount of lithium. Using this method, the cycle life of the cell was determined over a short period simply from the lithium cycling efficiency. The lithium cycling efficiency in $LiAsF_6$–2MeTHF/EC was improved by removing both water and organic impurities such as peroxides. An electrolyte containing less than 14 ppm of water and 20 ppm of organic impurities had a high lithium cycling efficiency of 97.2%.

1. Introduction

Recently, rechargeable cells with lithium ion doped carbon anodes have been widely used as the high energy density power sources of such portable devices as cellular phones and video-camcorders. By contrast, rechargeable cells with lithium metal anodes (referred to as 'lithium metal cells') are still attractive because theoretically they have a higher energy density than lithium ion cells. However, practical lithium metal cells have not been marketed because of their poor cyclability and safety problems. In the late 1980s, Moli Energy Co. of Canada developed AA lithium metal cells. The cycle life of these cells was improved by controlling the lithium deposition morphology during charging by applying mechanical stack pressure to the anode and by using $LiAsF_6$-based electrolytes [1]. More recently Tadiran Co. of Israel reported to develop their development of AA lithium metal cells with improved safety [2]. These reports suggest the possibility of realizing practical lithium metal cells with excellent cyclability and safety.

Lithium metal is very reactive with organic electrolytes, and passive films are formed on the lithium surface as reaction products. It is widely recognized that the properties of these passive films affect lithium cyclability [3]. The passive film composition depends on the composition of the organic electrolyte. The relationship between organic electrolyte composition and lithium metal cell cyclability is usually evaluated in terms of lithium cycling efficiency (E_{ff}). Lithium cycling efficiency is defined as the ratio of discharge capacity to charge capacity. When the characteristics of organic electrolytes are discussed, lithium half cells [4] are mainly used to evaluate lithium cyclability because of their simple cell structure and the short time needed for evaluation. However, the lithium cycling efficiencies obtained from half cells are not always consistent with those obtained from cells with both a cathode and an anode (referred to as 'full cells' in contrast with 'half cells') [5]. This may be because the morphology of deposited lithium in the full cells and half cells is different, and because traces of cathode material may dissolve in the electrolyte and be deposited on the lithium anode. By contrast, it takes at least several months to evaluate lithium cyclability using full cells.

We have already reported that 2-methyltetrahydrofuran (2MeTHF)/ethylene carbonate (EC) mixed solvent organic electrolytes exhibit good lithium cycling efficiencies, this being due to the lithium surface film formation being able to cycle lithium better than 2MeTHF single solvent electrolyte [6]. In this work we investigate the effect of purifying the organic electrolyte on lithium cyclability. This investigation was carried out by using a new accelerated method for measuring lithium cyclability. This method involves a cycle test of the coin cell which has both a cathode and a small amount of lithium anode. We used an amorphous V_2O_5–P_2O_5 (95:5 molar ratio) as the cathode [6]. The tests were usually completed within a week and the results correlated relatively well with those obtained from full cell tests.

2. Experimental details

2.1. *Solvent purification*

2MeTHF (Tomiyama Pure Chemical Co.) was distilled after desiccating it with CaH_2 overnight and then refluxed in an Ar gas atmosphere for half a day. The reflux ratio was 20:1, and a 60% portion of distilled 2MeTHF was obtained as the main flux. Distilled 2MeTHF was passed through an activated alumina (Woelm neutral 200 W, activity: super I) column in an Ar gas flow glove-box to remove traces of peroxide from the distilled 2MeTHF. 1 g of activated alumina was used for 5 ml of 2MeTHF [7]. By this treatment, neither polymerization, decomposition, increase in viscosity nor colouring was observed.

EC, purchased from the Wako Chemical Co., was purified in a room whose temperature was controlled at 40 °C to prevent crystallization. The melting point of EC is 36 °C and so it was desiccated with 4A type molecular sieves, which were activated at 400 °C for 4 h before distillation. Distillation was carried out in vacuum (about 7 torr) at a 20:1 of reflux ratio.

2.2. *Preparation of organic electrolytes*

Commercially obtained $LiAsF_6$ (Lithcoa Co.) was used as the electrolyte salt after drying it at 80 °C or less in vacuum (7×10^{-7} torr).

2.3. *Organic electrolytes preparation*

Purified 2MeTHF and EC were mixed at a volume ratio of 1:1, and cooled to about 0 °C. Small amounts of $LiAsF_6$ (0.5–1.0 g) were dissolved several times in 100 ml of mixed solvent which was stirred with a magnetic stirrer to avoid the $LiAsF_6$ from being decomposed by the heat of the dissolution. The organic electrolytes were desiccated by passing them through an activated alumina column (Woelm, neutral 200 W) to remove traces of water contained in $LiAsF_6$. 1 g of alumina was used for 5 ml of electrolyte. The lithium ion concentration before and after the column preparation, was analysed with an ICP spectrometer (Shimazu Co., model AA670). The moisture in the electrolytes was analysed with a Karl–Fisher Analyser (Kyoto Electrical Industry Co.). Titer of the Karl–Fisher agent (Mitsubishi Chemical Co.) was 0.5.

2.4. *Test cell preparation*

Figure 1 is a schematic drawing of a coin type test cell (23 mm diameter and 2 mm thick) consisting of a cathode, an anode (lithium metal), a separator, a cathode cap, an anode cap and a gasket ring. We used amorphous V_2O_5–P_2O_5 (95:5 in molar ratio, i.e., 95 mol % V_2O_5; a-V_2O_5) as the cathode active material because it has excellent charge–discharge reversibility [6]. The a-V_2O_5 was prepared by melting reagent-grade raw oxides in platinum crucibles for 1 h at 750 °C, and then quenching them on a water-cooled iron block [6]. The a-V_2O_5 was then mixed with acetylene black (Denkikagaku Kogyou Co.) and poly tetrafluoro-ethylene at a weight ratio of 70:25:5 and formed into a sheet with a roll press. This cathode sheet was then punched into 17 mm diameter disks. The cathode discs were covered with a titanium net and attached to cathode cases by spot welding the titanium net. The anode was formed by pressing a 17 mm diameter and 0.05 mm thick piece of lithium foil into the anode cap. The anode capacity was 15 mAh and the cathode capacity down to a discharge voltage of 2.0 V was 20 mA h. A 19 mm diameter Celgard 2502 (Cellanese Co.) was used as a separator.

2.5. *Electrochemical measurement*

Charge–discharge cycle tests on the lithium/a-V_2O_5 cells were carried out galvanostatically using cell cyclers (Hokutodenko Co.) between charge and discharge cut-off voltages of 3.5 and 2.0 V, respectively, and with a discharge and a charge current of 1 mA (0.5 mA cm^{-2}), with a rest of 1 h between charging and discharging.

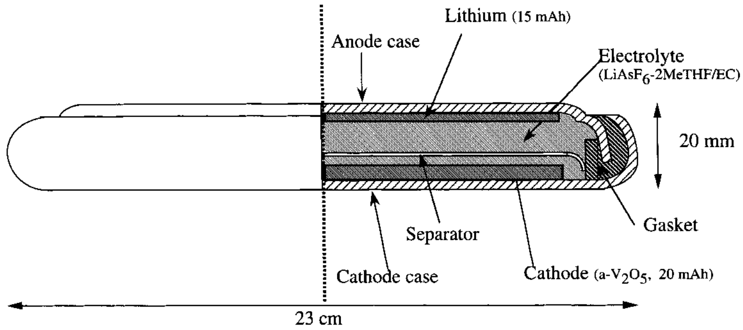

Fig. 1. Schematic drawing of the construction of the coin cell for the accelerated test.

2.6. *Analysis of solvent impurities*

The impurities in the solvents were analysed with a gas chromatograph (Shimazu Co., model GC-6A) and a gas chromatograph mass spectrometer (Jeol Co.). The measurement conditions are given in Table 1.

3. Results and discussion

3.1. *Determination of $LiAsF_6$ desiccation conditions*

Figure 2 shows the relationship between $LiAsF_6$ desiccating temperature and the water content of the electrolyte. The $LiAsF_6$ was desiccated in vacuum (2×10^{-6} torr) for 48 h and then dissolved in 2MeTHF to form a 1.5 mol l^{-1} (M) solution to enable measurement of the water content of the electrolytes. The water content decreased with an increase in the desiccating temperature and reached a maximum around 100 °C. The $LiAsF_6$ desiccated at 150 °C changed from white to grey, which suggests electrolyte decomposition. The product of this decomposition (acid) may react with the Karl–Fisher agent resulting in an apparent increase in the water content over 150 °C:

$$AsF_5 + C_5H_5N \rightarrow C_5H_5N{:}AsF_5 \tag{1}$$

$$2\,C_5H_5N{:}AsF_5 + I_2 \rightarrow 2\,C_5H_5\underset{\diagdown \mathrm{I}}{N} - AsF_5 \tag{2}$$

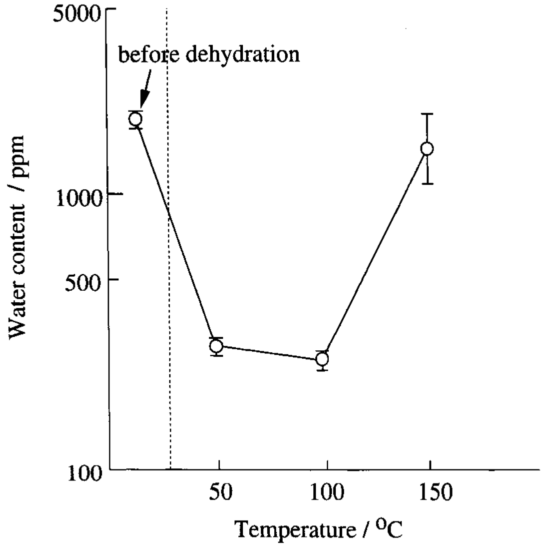

Fig. 2. Relation between water content and drying temperature for $LiAsF_6$.

3.2. *Impurities in 2MeTHF and its purification*

Figure 3(a) shows a gas chromatogram of the purchased 2MeTHF which contained impurities such as acetone, 2-ethoxy butane, *n*-propyl acetate, 5-methyl tetrahydrofurfuryl alcohol and butanol. These impurities were removed by distillation as shown in Figure 3(b). However, 2MeTHF also contains 2-methyl furan (2MeF) of which 0.2 ~ 0.4 vol % reportedly remains after distillation [8]. The 2MeF content was analysed using 12.5 m of OV-1 capillary column. Also, it was found that the 2MeF as-purchased contained 6000–10000 ppm of 2MeF which was reduced to 1000 ppm by fine distillation. Hydrogen gas was bubbled through the finely distilled 2MeTHF with a Pt powder for one day at room temperature to remove as much of the 2MeF as possible. As a result the content was reduced to 20 ppm. The electrolyte turned pink, which suggested that peroxide was formed in the distilled 2MeTHF despite it being kept for a long time in an Ar gas flow glove-box. Unfortunately, it was not possible to determine the peroxide content from the GS-mass spectrum because of the complicated fragmentation of the mass peak. No distilled 2MeTHF that was more than a few weeks old was used.

Table 1. Gas chromatography measurement conditions

Sample	Column	Injection room temp. /°C	Column oven temp. /°C
2MeTHF	PEG 20M (3 m, glass)	100	30
	PEG 20M (25 m, 0.3 mm dia. capillary)	100	30
	OV-1 (12.5 m, 0.2 mm dia. capillary)	150	50
EC	PEG 20M (1 m, glass)	140	130
	PEG 20M (25 m, 0.3 mm dia. capillary)	140	130

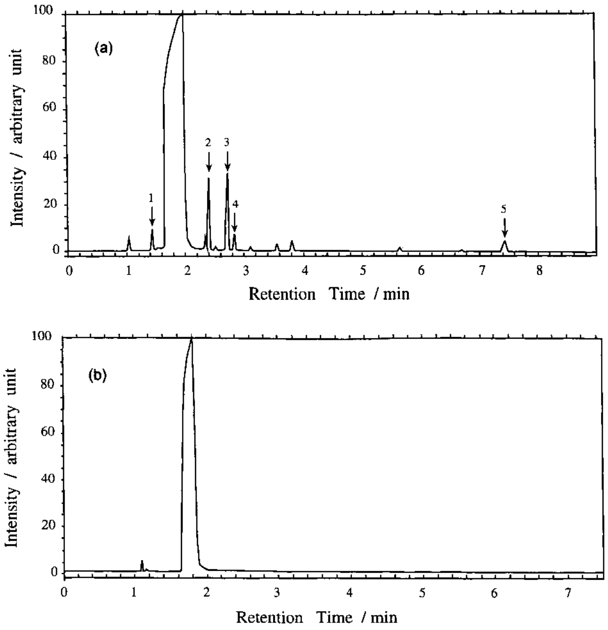

Fig. 3. Gas chromatograms (a) of received 2MeTHF. Key: (1) acetone, (2) 2-ethoxy-butane, (3) *n*-propylacetate, (4) tetrahydro-5-methyl-fufurylalcohol and (5) 1-butanol; (b) of purified 2MeTHF.

3.3. *Impurities in EC and its purification*

Ethylene glycol and ethylene glycol-1-formate were identified as EC impurities as shown in Figure 4(a). the ethylene glycol was removed by fine distillation, however, the ethylene glycol-1-formate could not be removed in this way. It was removed by adsorption using molecular sieves 4A (Figure 4(b)).

3.4. *Evaluation of lithium cyclability using accelerated tests*

Lithium cycling efficiency (E_{ff}) defined as the ratio of discharge capacity to charge capacity is usually adopted for the evaluation of lithium cyclability using lithium half cells and full cells. However, as mentioned above, the results of half cell tests are sometimes different from those of full cells. However, it takes several months to complete full cell tests.

The authors propose a new way to evaluate E_{ff} by using an accelerated method in which the cell configuration is the same as that of full cells except for the anode capacity. Moreover, it takes only a week at most to evaluate E_{ff} using this method. A key feature of this method is that the anode has a very small capacity compared to the cathode. When charge–discharge cycle tests are carried out using these cells, a capacity decline corresponding to E_{ff} must be observed as shown in the following equations. If E_{ff} is independent of the $(n-1)$th discharge capacity (C_{n-1}), C_n is expressed by Equation 3:

$$C_n = E_{\mathrm{ff}}\, C_{n-1} = E_{\mathrm{ff}}^{n-1}\, C_1 \tag{3}$$

where C_1 is the first discharge capacity. Thus,

$$\log C_n - \log C_1 = (n-1)\log E_{\mathrm{ff}} \tag{4}$$

However, cathode active materials are needed which do not change their capacity and structure during the charge–discharge cycles for adoption of this method for the evaluation of E_{ff}. Figure 5 shows a preliminary charge–discharge cycle test result for a lithium/amorphous V_2O_5(a-V_2O_5) coin cell. In this cell, the anode capacity of 15 mA h is less than the cathode capacity of 20 mA h. The use of the amorphous cathode led to an approximately linear decrease in the discharge voltage with an increase in discharge time. The voltage profile of the Li/a-V_2O_5 cell did not change with increase in cycle number, although the discharge capacity faded. In this cell, the capacity fade is determined only by the lithium consumption. This means that a-V_2O_5 can be a suitable cathode active material for the proposed method.

The figure of merit (FOM) of a lithium electrode is the number of times that a given quantity of lithium can be reused in successive charge–discharge cycles, and is related to E_{ff} by Equation 5.

$$\mathrm{FOM} = \frac{1}{1 - E_{\mathrm{ff}}} \tag{5}$$

Thus it is possible to recognize an improvement in lithium cyclability as an improvement in cell cycle life by using FOM instead of E_{ff}. When E_{ff} increases from 0.98 (98%) to 0.99 (99%), FOM increases from 50 to 100 which means a doubling of the cycle life. FOM is easier to understand and a more practical way of determining the number of cycles in the cycle life than E_{ff}. Therefore, FOM was used to evaluate lithium cyclability in this work.

3.5. *Effect of electrolyte purification on lithium cyclability*

The effect of $LiAsF_6$–EC/2MeTHF electrolyte purification on the lithium cyclability was examined.

3.5.1. *Effect of water content*

$LiAsF_6$ is hydroscopic and the electrolyte solution was passed through an alumina column after $LiAsF_6$ has

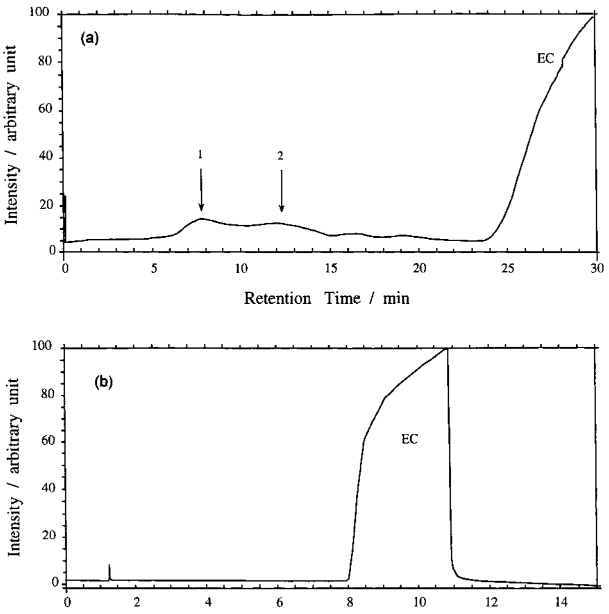

Fig. 4. Gas chromatograms (a) of received EC and (b) of purified EC. Key for (a): (1) ethylene glycol-1-formate and (2) ethylene glycol.

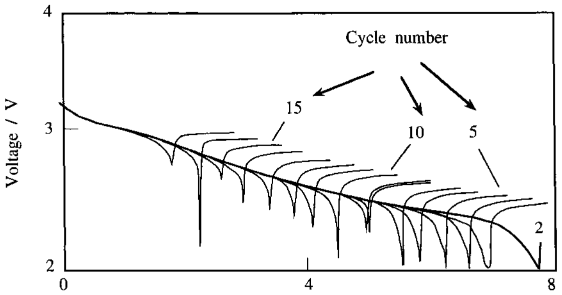

Fig. 5. Discharge curves of a cell whose lithium capacity is less than that of a a-V_2O_5 cathode.

been dissolved in 2MeTHF/EC mixed solvent to remove any traces of water. It is possible to reduce water content to below 20 ppm by this procedure.

Figure 6 and Table 2 show the effect of water content on lithium cyclability. In this figure, the x-axis is the cycle number and the y-axis is the discharge capacity on a logarithmic scale. E_{ff} values were obtained from the slope of an interpolated linear segment. The FOM became larger with a decrease in water content. Organic electrolyte containing 27 ppm of water had an FOM of 29, while one containing 117 ppm of water had an FOM of 23. Electrolyte containing 370 ppm of water had an extremely low value of 2.6. The 2MeF content varied for the electrolytes shown in Table 2, and the influence of the 2MeF content was negligible, as explained later. A decline in lithium cyclability with an increase in water content was also reported for $LiClO_4$–2MeTHF [9] while an improvement in lithium cyclability was also reported in $LiClO_4$- or $LiAsF_6$-propylene carbonate with traces of water [10]. The effect of water on lithium cyclability may depend on the sort of solvents and electrolyte salts that are used. In the $LiAsF_6$–2MeTHF/EC systems examined here, the FOM improved with a decrease in water content. The cause of the decline could be the formation of LiOH on the lithium anodes as reported in FTIR studies [11].

3.5.2. *Effect of organic impurities*

Figure 7 and Table 3 show the effect of organic impurities other than 2MeF on the lithium cyclability using organic electrolytes containing 130 ppm of water. The FOM values were 16.1 and 14.8 for organic electrolytes containing 6500 ppm and 23 400 ppm of organic impurities, respectively. A solution containing 1030 ppm of organic impurities and 117 ppm water had an FOM of 23. The FOM tended to decrease with an increase in organic impurities. The capacity fade in the first few cycles was much quite larger in the organic electrolyte containing 23 400 ppm of organic impurities than in that containing 6500 ppm. As shown in Figure 6, the differences in water content caused no great reduction in the capacity in the first few cycles but there was a large reduction in the FOM. These differences in lithium cycling behavior with changes in water or organic impurity content may be caused by differences in the rate of the reaction between the lithium and the impurities. The lithium may react slowly with the water or the lithium surface may be passivated once the lithium has reacted with the water. By contrast, the reaction rate of lithium with organic impurities such as peroxide may be fast.

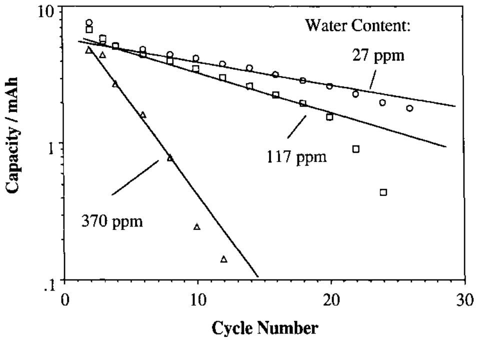

Fig. 6. FOM dependence on the water content of the electrolytes.

Table 2. Relationships between water content and FOMs

Impurities/ppm			Efficiency, E_{ff} /%	FOM = $1/(1 - E_{ff})$
Water	2MeF	Others		
27	20	30	96.6	29
117	970	30	95.7	23
370	970	32	61.5	2.6

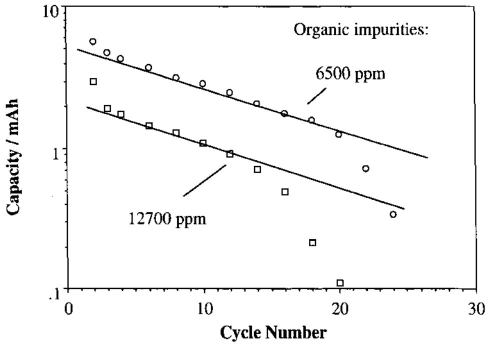

Fig. 7. FOM dependence on organic content in the electrolytes.

3.5.3. *Effect of 2-methyl furan*

It is very difficult to separate 2MeF completely from 2MeTHF by distillation. However, an improvement in lithium cyclability in $LiAsF_6$–THF/2MeTHF by the addition of 2MeF has been reported [8]. This is because highly reactive 2MeF produces a suitable lithium surface film for cycling lithium well [12]. Therefore, it is important to investigate the effect of 2MeF in $LiAsF_6$–2MeTHF/EC. Figure 8 and Table 4 show the effect of 2MeF in $LiAsF_6$–2MeTHF/EC which contains 27 ppm of water and 30 ppm of other organic impurities. The FOM values were 29 and 30 for organic electrolytes containing 20 and 1000 ppm of 2MeF, respectively. In addition, a slight decline in capacity during the first several cycles was observed for the organic electrolyte containing 10 000 ppm of 2MeF. 2MeF had no significant effect on the lithium cyclability for $LiAsF_6$–2MeTHF/EC organic electrolyte. This shows that EC plays a similar role in the 2MeTHF/EC system to 2MeF in the

Table 3. Relationships between organic impurity content and FOMs

Impurities/ppm			Efficiency, E_{ff} /%	FOM = $1/(1 - E_{ff})$
Water	2MeF	Others		
130	6200	6500	93.8	16.1
130	200	23400	93.2	14.8

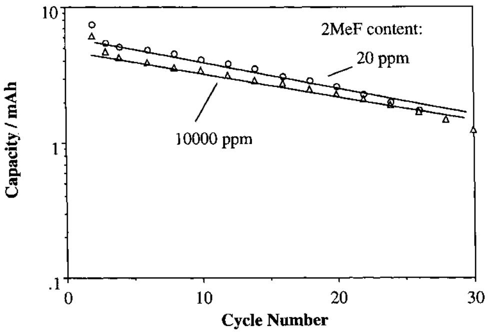

Fig. 8. FOM dependence on 2MeF content in the electrolytes.

Table 4. Relationships between 2MeF content and FOMs

Impurities/ppm			Efficiency, E_{ff} /%	FOM = $1/(1 - E_{ff})$
Water	2MeF	Others		
27	20	30	96.6	29
27	10000	30	96.7	30

2MeTHF/THF system without EC [8]. That is, the reactivity of EC itself rather than 2MeF may affect the lithium cycling efficiency via the production of suitable surface film. With $LiAsF_6$–EC/2MeTHF, the possible main chemical components in the lithium surface film are lithium alkoxide formed from 2MeTHF, lithium alkyl carbonates and lithium carbonate formed from EC and PC, LiF and lithium arsenic fluorides formed from $LiAsF_6$ [13].

3.5.4. *Organic electrolyte degradation*

There were some organic electrolytes which became pale pink when $LiAsF_6$ was dissolved in 2MeTHF/EC mixed solvent. These electrolytes became brown in a few days. The FOM of these coloured organic electrolytes was in the range $20 \sim 23$, while the FOM of ordinary organic electrolytes was in the range $26 \sim 29$. This degradation may be the result of peroxide formation in distilled 2MeTHF [14]. The degradation was avoided by using the finely distilled 2MeTHF mentioned above.

To summarize the results, the lithium cyclability was improved when both water and organic impurities were removed. Electrolytes containing less than 14 ppm of water, 10 ppm of organic impurities and 10 ppm of 2MeF had the highest FOM of 35.6 (lithium cycling efficiency of 97.2%) among the electrolytes we examined.

4. Conclusion

Accelerated tests were successfully carried out using *a*-V_2O_5 cathode which did not change its capacity or structure during charge-discharge cycles. Lithium cyclability was improved by removing both water and organic impurities such as peroxides. 2MeF caused no significant improvement in $LiAsF_6$–2MeTHF/EC. Electrolytes containing less than 14 ppm of water and 20 ppm of organic impurities had a high FOM of 35.6 (lithium cycling efficiency of 97.2%). Further purification is expected to improve lithium cyclability even more and $LiAsF_6$–2MeTHF/EC may be one of the most promising organic electrolytes for rechargeable cells with lithium metal anodes.

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