

## ORGANIC ADDITIVES FOR THE ELECTROLYTES OF RECHARGEABLE LITHIUM BATTERIES

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### Summary

The effects of some organic additives containing hetero-atoms on the charge-discharge characteristics of lithium have been investigated in propylene carbonate- or dimethylsulfoxide-based electrolytes. The addition of thiophene to propylene carbonate-based electrolytes improved the coulombic efficiency of the cycle, and the addition of pyrrole was effective for cycling in  $\text{LiPF}_6/\text{dimethylsulfoxide}$ . The effect of the addition of 2-methylfuran was significant in the solutions containing  $\text{LiPF}_6$ . The a.c. impedance behavior at the electrode/electrolyte interphase suggested that the addition effects are related to changes in the interphase structure.

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### Introduction

The key technology for the realization of ambient temperature, rechargeable lithium batteries with practical capacities is an improvement in the cycleability of the negative electrode. Many organic electrolyte systems have been proposed and examined for this purpose. Among them, addition effects of some organic compounds have been investigated recently. According to the first report concerning additives in organic electrolytes by the EIC group [1], the lithium cycling efficiency was markedly improved by the addition of 2-methylfuran (MF) to the  $\text{LiAsF}_6/2\text{-methyltetrahydrofuran}$  (MTHF) electrolyte. Analogous organic additives, especially unsaturated cyclic compounds, have thereafter been examined [2, 3].

It was considered that the improvement in the cycling efficiency by the addition of MF is due to the formation of an  $\text{Li}^+$ -ion conductive film at the surface of the lithium negative electrode [1, 2]. However, the mechanistic detail of this addition effect is still ambiguous. In this paper, the influences of the addition of several unsaturated cyclic compounds containing hetero-atoms have been investigated for propylene carbonate (PC)- and dimethylsulfoxide (DMSO)-based electrolytes.

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## Experimental

The base solvents of the electrolytes were PC and DMSO. In some experiments tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) was used as a co-solvent of PC and DMSO. These were battery grade solvents (Mitsubishi Yuka) or special grade reagents (Tokyo Kasei Kogyo), these latter being further dehydrated and purified by distillation procedures. The electrolytic salts were  $1 \text{ mol dm}^{-3}$  (M) of  $\text{LiClO}_4$  (Ishizu Pharmaceutical) and  $\text{LiPF}_6$  (Morita Chemical Industries). The additives were MF, thiophene (Tp), 2-methylthiophene (MTp), 2,5-dimethylthiophene (DTp), pyrrole (Py), and 4-methylthiazole (MTz). The concentrations of the additives ranged from 0.2 to 1.0 vol.%.

The coulombic efficiency of the lithium negative electrode was determined by a galvanostatic charge/discharge cycle on a nickel substrate [4]. The cycling current,  $i_{\text{ch}} = i_{\text{dis}}$ , was usually  $2 \text{ mA cm}^{-2}$ , and the charged capacity,  $Q_{\text{ch}}$ , was  $0.2 \text{ C cm}^{-2}$ . The electrochemical behavior of the additive was investigated by the current-potential curves measured at a lithium or glassy carbon (GC) electrode. The a.c. impedance technique was also employed to obtain information on the lithium/electrolyte interphase. All experiments, including the electrolyte preparation, were carried out under a dry Ar atmosphere at room temperature ( $16 - 22^\circ \text{C}$ ).

## Results and discussion

A typical effect of an addition on the lithium cycling efficiency at a nickel substrate is shown in Fig. 1, where 0.5 vol.% of Tp was added to  $\text{LiClO}_4/\text{PC}$  or  $\text{LiPF}_6/\text{DMSO}$ . The addition of Tp to  $\text{LiClO}_4/\text{PC}$  improved the lithium cycleability and prevented the efficiency from decreasing with

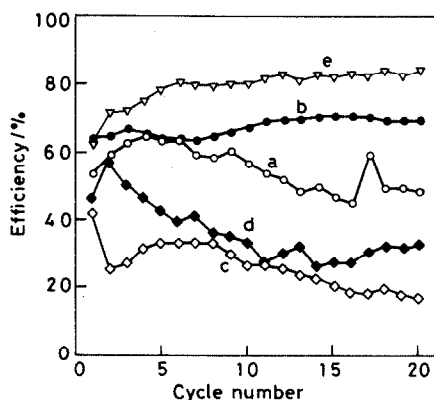


Fig. 1. Variation of the efficiency with cycle number. a:  $\text{LiClO}_4/\text{PC}$ ; b:  $\text{LiClO}_4/\text{PC} + \text{Tp}$ ; c:  $\text{LiPF}_6/\text{DMSO}$ ; d:  $\text{LiPF}_6/\text{DMSO} + \text{Tp}$ ; e:  $\text{LiPF}_6/\text{DMSO} + \text{DME}(1:1)$ .  $i_{\text{cy}} = 2 \text{ mA cm}^{-2}$ ,  $Q_{\text{ch}} = 0.2 \text{ C cm}^{-2}$ .

repeated cycling (curves a and b). However, the addition of Tp to  $\text{LiPF}_6/\text{DMSO}$  had little effect (curves c and d). The improvement in efficiency following Tp addition was also less than that by solvent mixing of DMSO with DME (1:1 by volume, curve e). Further addition of Tp to the blended DMSO–DME system decreased the efficiency somewhat.

The addition of MTp or DTp to  $\text{LiClO}_4/\text{PC}$  solution was effective but the introduction of methyl group(s) to Tp had no significant effect on efficiency. In general, there were optimum values for the concentrations of the additives (ca. 0.2 - 1.0 vol.%).

Figures 2 and 3 show, respectively, the addition effects of MF and Py on lithium cycling efficiency. Here, the additive concentrations were 0.5 vol.% with regard to the electrolyte solution. MF, which was an effective additive to the  $\text{LiAsF}_6/\text{MTHF}$  electrolyte [1, 2], showed little improvement in the  $\text{LiClO}_4/\text{PC}$  system. However, the addition of MF to the  $\text{LiPF}_6/\text{DMSO}$  solution improved the efficiency to a considerable extent. In the case of Py addition, the efficiency in  $\text{LiClO}_4/\text{PC}$  decreased with increasing Py concentration, but the efficiency in  $\text{LiPF}_6/\text{DMSO}$  was improved by the addition of Py. The efficiency in  $\text{LiPF}_6/\text{DMSO}$  to which Py had been added changed slightly with repeated cycling and its average efficiency (0 - 20th cycle) was about 75%. The effect of MTz, except for other than when it was added to  $\text{LiPF}_6/\text{PC}$ , was generally small.

Consequently, the addition effects of these compounds were shown to be different for different organic electrolyte systems. These results suggest that the addition effects of these compounds are based on the different reactions with each other. However, there might be some similarity in the effects between the electrolyte/additive combinations of  $\text{LiAsF}_6/\text{MF}$  [1 - 3] and  $\text{LiPF}_6/\text{MF}$ , the former being thought to form an  $\text{Li}^+$ -conductive film containing an  $-\text{As}-\text{O}-$  component with a polymeric matrix.

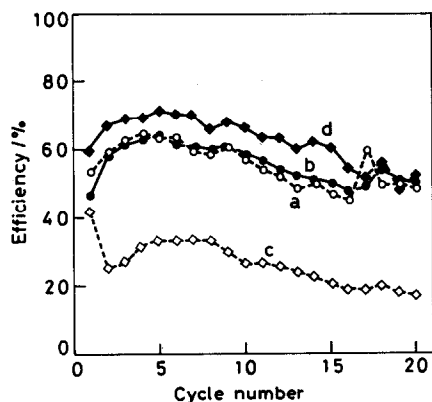


Fig. 2. Variation of the efficiency with cycle number. a:  $\text{LiClO}_4/\text{PC}$ ; b:  $\text{LiClO}_4/\text{PC} + \text{MF}$ ; c:  $\text{LiPF}_6/\text{DMSO}$ ; d:  $\text{LiPF}_6/\text{DMSO} + \text{MF}$ .  $i_{\text{cy}} = 2 \text{ mA cm}^{-2}$ ,  $Q_{\text{ch}} = 0.2 \text{ C cm}^{-2}$ .

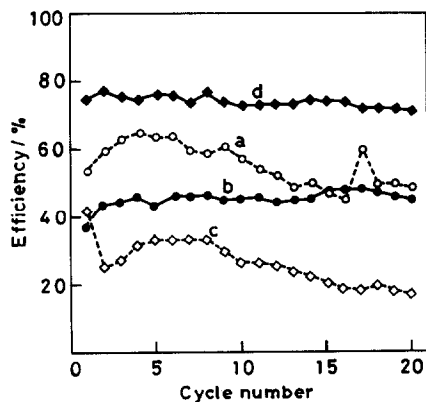


Fig. 3. Variation of the efficiency with cycle number. a:  $\text{LiClO}_4/\text{PC}$ ; b:  $\text{LiClO}_4/\text{PC} + \text{Py}$ ; c:  $\text{LiPF}_6/\text{DMSO}$ ; d:  $\text{LiPF}_6/\text{DMSO} + \text{Py}$ .  $i_{\text{cy}} = 2 \text{ mA cm}^{-2}$ ,  $Q_{\text{ch}} = 0.2 \text{ C cm}^{-2}$ .

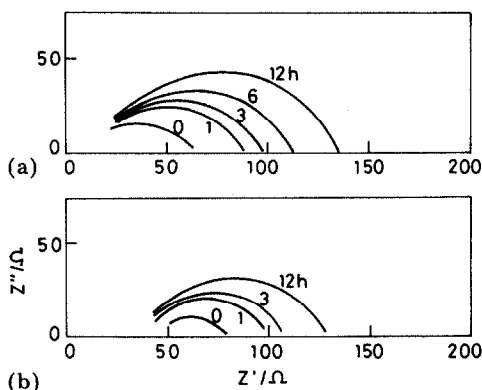


Fig. 4. Cole-Cole plots of the a.c. impedance at the lithium electrode in  $\text{LiClO}_4/\text{PC}$  (a) and  $\text{LiClO}_4/\text{PC} + \text{Tp}$  (b). Frequency was scanned from 50 kHz to 0.1 Hz. Figures on the curves indicate the immersion time.

The addition of Tp was only effective in the PC-based electrolytes. Figure 4 shows Cole-Cole plots of the a.c. impedance at lithium in  $\text{LiClO}_4/\text{PC}$  as a function of the time after anodic dissolution of the surface in the same electrolyte. The diagrams consisted of single semicircles. The radius of the semicircle, which is equivalent to the resistive component at the interphase, increased with time of electrode immersion in the electrolyte. The addition of Tp to  $\text{LiClO}_4/\text{PC}$  reduced the growth of the semicircle with time. This suggests that Tp suppresses the growth of the less-conductive film formed on the lithium surface in the  $\text{LiClO}_4/\text{PC}$  electrolyte [5].

The reactivity of the additive with lithium metal was evaluated by its oxidation potential [6] measured by voltammetry at a GC electrode. In PC-based electrolytes, the order of reactivity was  $\text{Tp} > \text{MF} > \text{Py}$  [7]. This agreed with the order of cycling efficiency in  $\text{LiClO}_4/\text{PC}$  electrolyte. That is, the improvement of the cycling efficiency in  $\text{LiClO}_4/\text{PC}$  as a result of the addition of Tp apparently relates to a chemical reaction of Tp with deposited lithium.

On the other hand, the exchange current density,  $i_0$ , for the deposition-dissolution reaction of lithium, eqn. (1), in the Tp- or Py-added  $\text{LiClO}_4/\text{PC}$  electrolyte was evaluated by the steady-state polarization of lithium [7].



Table 1 summarizes the apparent  $i_0$ s (with respect to the apparent surface area) calculated from the slopes of the current-potential curves. The addition of Tp to  $\text{LiClO}_4/\text{PC}$  slightly reduced  $i_0$  (i.e., increased the polarization resistance), whereas the Py addition led to an increase in the apparent exchange current density. Compared with the results shown in Figs. 1 and 4, Tp seems to strongly adsorb and/or to form a protective film at the lithium surface in  $\text{LiClO}_4/\text{PC}$ . The adsorption of Tp probably suppresses

TABLE 1

Apparent exchange current density ( $i_0$ ) measured by the steady-state polarization method in  $\text{LiClO}_4$  (1 mol  $\text{dm}^{-3}$ )/PC

Additives (2 cm <sup>3</sup> dm <sup>-3</sup> )	$i_0$ (10 <sup>-5</sup> A cm <sup>-2</sup> )
None	2.6
Thiophene	2.2
Pyrrole	4.2

the growth of a non-conductive film formed by the reaction of lithium with PC containing  $\text{LiClO}_4$ . Even if film formation occurs as a result of the reaction of Tp with lithium, it may reduce the surface roughness during the deposition-dissolution cycles. By contrast, the enhancement of the apparent current by the addition of Py may be caused by an increase in the real surface area of the lithium electrode. A very rough lithium surface is highly reactive to organic compounds, which leads to a decrease in the coulombic efficiency of lithium.

In the DMSO-based electrolytes, however, there was no clear relation between the improvement in efficiency and the reactivity of the additives. This would be due, partly, to the different mechanism for the loss of lithium cycling efficiency in the DMSO-based electrolytes from that in the PC-based solutions. Further investigations involving the electrolyte additives are now in progress and results will be presented elsewhere.

## References

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