Effects of quinoneimine dyes on lithium cycling efficiency for LiClO₄-propylene carbonate

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Additive effects of quinoneimine dyes (QIDs) on Li cycling efficiency (E_{ff}) were examined in 1 M LiClO₄-propylene carbonate (PC). The E_{ff} values were measured galvanostatically on a Pt working electrode. The E_{ff} values for solutions with QID addition were higher than those for PC alone and the E_{ff} values depended on cycling current density and on the amounts of QID added. For example, 1 M LiClO₄-PC with added methylene blue (MB) (10^{-3} M addition) showed E_{ff} values exceeding 90% at 0.5 mA cm^{-2}, 0.6 C cm^{-2}, while the E_{ff} values for PC alone were approximately 65%. From observation with a scanning electron microscope the morphology for the deposited Li in solution with MB added was found to be smoother than that in PC alone. The E_{ff} values for solutions with QID added tended to increase with an increase in the reduction potential for QID vs Li–Li$^+$. The enhancement of the Li cycling efficiency by QID addition seems to be caused by Li$^+$ ion-conductive film formation on the deposited Li surface, resulting from the reaction between QID and the deposited Li, that suppresses the reaction between PC and the deposited Li. This film formation was strongly suggested by the measurement of the resistance on the Li surface.

1. Introduction

Efficient electroplating and stripping of Li in non-aqueous media is essential to the development of ambient-temperature secondary lithium batteries. Propylene carbonate (PC) is the most common media for lithium batteries. However, Li cycling efficiency in PC is not high enough for practical application in secondary lithium batteries due to the formation of an electrochemically inert Li compound resulting from the reduction of PC by the deposited Li [1]. Two methods have been proposed for improving Li cycling efficiency for PC by suppressing the PC-Li reaction.

The first method is the addition of compounds which are kinetically more stable towards Li and which have higher solvation power for Li$^+$ than PC, such as N, N, N′, N′-tetramethylethylenediamine [2] and tetrahydrofuran [3]. The improvement in Li cycling efficiency obtained by this method is explained by the adsorption of less-Li-reactive compounds on the deposited Li.

The second method is the addition of compounds more reactive to Li than PC, such as SO₂, H₂O and CH₃NO₂ [4]. The improvement in Li cycling efficiency obtained by this method is attributed to the formation of a Li$^+$ ion-conductive film on the deposited Li.

This work reports the additive effects of quinoneimine dyes (QIDs) on Li cycling efficiency for LiClO₄-PC solutions. The general chemical structure for QIDs is shown in Fig. 1 and Table 1. QIDs are heterocyclic aromatic compounds. The reason for the use of QIDs as additives is that they can be used as the cathode active materials for non-aqueous lithium cells even though they are soluble in PC, as we
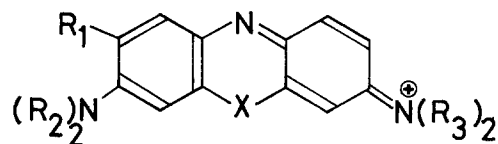

Fig. 1. General chemical structure for quinoneimine dye (QID); counter anion is Cl$^-$.

Table 1. Structure of quinoneimine dyes shown in Fig. 1

Compounds	R_1	R_2	R_3	X
Methylene blue (MB)	H	CH_3	CH_3	S
Neutral red (NR)	CH_3	H	CH_3	NH
Capri blue (CB)	CH_3	C_2H_5	CH_3	O
Toluidine blue (TB)	CH_3	H	CH_3	S
Methylene green (MG)	H	CH_3	CH_3	S

previously reported [5]. The results indicate the possibility of Li^+ ion-conductive film formation as in the case of pyromellitic dianhydride [6]. If the Li^+ ion-conductive film is formed by addition of QID to PC it will be expected to improve Li cycling efficiency.

2. Experimental details

2.1. Electrolytes

PC (Tokyo Kasei Co.) was distilled at approximately 4 mm Hg pressure and 108° C. $LiClO_4$ (Kanto Chemicals Co.) and QID (Tokyo Kasei Co.) were employed after drying in a vacuum at 160° C and 60° C, respectively. Electrolytic solutions were prepared by mixing adequate amounts of solute, solvent and QID. The water contents of the electrolytes were measured by the Karl Fischer method and found to be less than 20 ppm.

2.2. Measurements

Lithium charge–discharge tests were galvanostatically carried out with a Rauh-type cell [7] at a temperature of $25 \pm 1°$ C. This cell, with approximately 2 ml of solution, was constructed with a Li counter electrode (20 mm diameter $\times 0.5$ mm), a Li reference electrode and a Pt working electrode (20 mm diameter $\times 0.5$ mm). The lithium charge–discharge efficiency was obtained from the stripping charge–plating charge using a 0.8 V potential cut-off as the stripping end point [7].

Scanning electron microscope (SEM) studies on the deposited Li were carried out as follows. Lithium was deposited on the Al holder for SEM observation (the deposited surface area was approximately $0.13 \, cm^2$) and the deposited

Li was rinsed in an Ar-filled drybox with dry 2-methytetrahydrofuran which has been reported to be the most stable solvent for Li [8]. The sample in a sealed glass container was transferred to a second drybox which was connected to the prevacuum chamber of the JSM-T JEOL scanning electron microscope.

Resistance on the Li surface in $LiClO_4$-PC with and without methylene blue was measured by the coulostatic method, details of which are reported elsewhere [5].

Preparations of the electrolytic solutions and all the tests were carried out in an Ar-filled drybox.

3. Results and discussion

3.1. *Li cycling efficiency for PC with added QID*

Fig. 2 shows the relation between the charge–discharge cycle number and Li cycling efficiency (E_{ff}) for 1 M $LiClO_4$-PC with and without QID (10^{-3} M addition) at 0.5 mA cm^{-2}, 0.6 C cm^{-2} on the Pt working electrode. The E_{ff} values for solutions with QID added were higher than those for PC alone. The degree of the decrease in E_{ff} values with increase in cycle number for PC with QID was smaller than that for PC alone. For example, 1 M $LiClO_4$-PC with methylene blue (MB) showed E_{ff} values exceed-
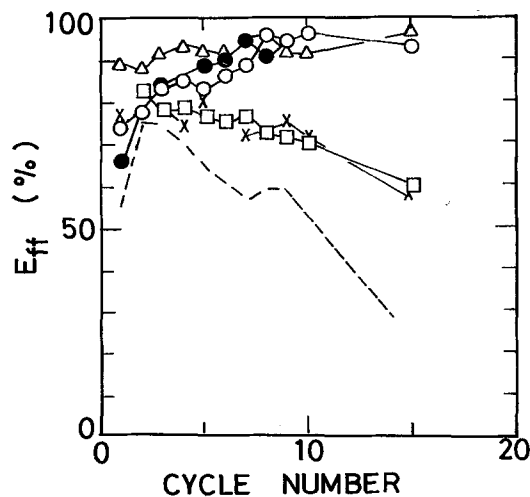

Fig. 2. Relation between Li cycling efficiency (E_{ff}) and cycle number for 1M $LiClO_4$-PC with (10^{-3} M) and without QID at 0.5 mA cm^{-2}, 0.6 C cm^{-2} on the Pt working electrode. △, MB; ●, TB; ○, NR; ▫, NR; □, MG; $\times$, CB; – – –, PC alone.
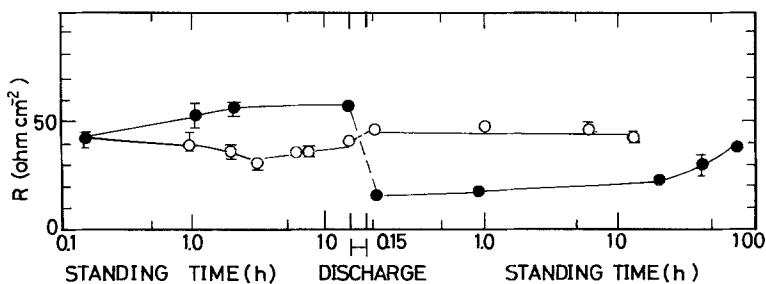
Fig. 3. Resistance (R) on the Li surface, 1 M $LiClO_4$. ○, PC with MB $(8 \times 10^{-4}M)$; ●, PC.

ing 90% up to the 15th cycle while the E_{ff} values for PC alone were less than 50% past the 10th cycle. There are two possible reasons for the enhancement of Li cycling efficiency for PC with a QID; i.e. the suppression of the reaction between PC and the deposited Li by (1) adsorption of a QID on the deposited Li surface and by (2) Li^+ ion conductive film formation on the deposited Li surface. When a QID exists around the deposited Li, the QID and Li react. This is because QIDs are reported [5] to be strongly reactive to Li with a reduction potential vs $Li-Li^+$ of more than 2.0 V. Therefore, the Li^+ ion-conductive film formation resulting from the QID–Li reaction is considered to be more likely than the adsorption of a QID on the deposited Li surface. To support this explanation resistance on the Li surface was measured for $LiClO_4$-PC with and without MB.

The resistance (R) on the Li surface in $LiClO_4$-PC with and without MB is shown in Fig. 3. For simple standing of the Li in PC alone, R increased with increase in standing time. This change in R reflects the gradual formation of Li_2CO_3 resulting from the reduction of PC by Li, as reported by Dey [9]. In the case of PC with MB, R gradually decreased with increase in time. These results, shown in Fig. 3, indicate that the film on the Li in PC with MB is different from that in PC alone.

The points connected with the broken lines in Fig. 3 show the changes of R values before and after discharge. Discharge was carried out at 0.32 mA cm^{-2}, 0.32 C cm^{-2}. In PC alone, R rapidly decreased after discharge and increased again with increase in standing time. The explanation for these results is that the Li_2CO_3 film is broken by discharge and a pure Li surface appears which causes the decrease in R after discharge. Pure Li reacts with PC again during

standing, which again causes an increase in R. In the case of solution with MB added the R values did not change before or after discharge or during the subsequent standing. These results indicate the possibility that the film formed in PC with MB added is an Li^+ ion-conductive film. The composition of this film is not clear. However, reductants of MB by Li, i.e. adducts of Leico-MB and LiCl [5], may be possible because of the easier reactivity of MB to Li(2.85 V vs $Li-Li^+$ [5]) than that of PC(0.6 V vs $Li-Li^+$ [9]).

3.2. E_{ff} dependence on amounts of MB added

The dependency of the E_{ff} values on the amount of MB added was examined. MB was added to PC in the range 10^{-6} to 10^{-1} M.
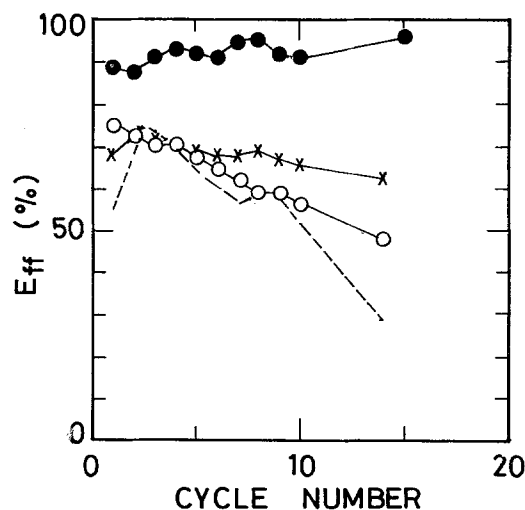

Fig. 4. Relation between Li cycling efficiency (E_{ff}) and cycle number for 1 M $LiClO_4$-PC with and without MB at 0.5 mA cm^{-2}, 0.6 C cm^{-2} on the Pt working electrode. ×, 10^{-1} M MB; ●, 10^{-3} M MB; ○, 10^{-5} M MB; – – –, PC alone.
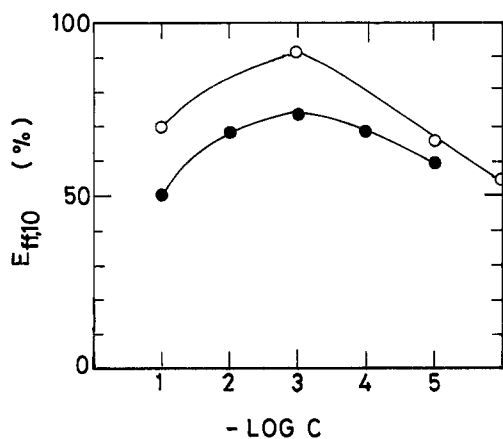
Fig. 5. Relation between average Li cycling efficiency ($E_{ff,10}$) and MB addition amounts (C, $mol\,l^{-1}$) for 1 M $LiClO_4$-PC, $0.6\,C\,cm^{-2}$ on the Pt working electrode. $\circ$, $0.5\,mA\,cm^{-2}$; $\bullet$, $5\,mA\,cm^{-2}$.

Fig. 6. Relation between Li cycling efficiency (E_{ff}) and cycling current density (I_{ps}) at a constant capacity of $0.6\,C\,cm^{-2}$ on the Pt working electrode, 1 M $LiClO_4$-PC with (10^{-3} M) and without QID. $\triangle$, MB; $\bullet$, TB; $\square$, MG; $\times$, CB; $\circ$, NR; —, PC alone.

Fig. 4 shows the relation between cycle number and Li cycling efficiency for 1 M $LiClO_4$-PC with and without MB at $0.5\,mA\,cm^{-2}$, $0.6\,C$ cm^{-2} on the Pt working electrode. Fig. 5 shows the dependence of the average Li cycling efficiency from the 1st to the 10th cycle ($E_{ff,10}$) on the amount of MB addition at $0.5\,mA\,cm^{-2}$ and $5\,mA\,cm^{-2}$ ($0.6\,C\,cm^{-2}$). The $E_{ff,10}$ values attained maxima at 10^{-3} M addition of MB for both $0.5\,mA\,cm^{-2}$ and $5\,mA\,cm^{-2}$. The reason for these phenomena is considered as follows. At less than 10^{-3} M addition the deposited Li surface is not entirely covered with MB-Li adducts. At addition of MB greater than 10^{-3} M excess adsorped MB produces resistance against the electrode reaction. The possibility of the adsorption of such a large ion species on the Li electrode has been reported in some other cases [10, 11].

3.3. E_{ff} dependence on cycling current density

The Li cycling efficiency dependence on Li cycling current density (I_{ps}) at a constant capacity of $0.6\,C\,cm^{-2}$ is shown in Fig. 6. In this case the E_{ff} values were those at the 1st cycle on the Pt working electrode [2]. The E_{ff} values in solutions with QID added attained maxima at $0.5\,mA\,cm^{-2}$, while the E_{ff} values in PC alone decreased with a decrease in I_{ps}, i.e. an increase in cycling time (T_{ps}). The results for PC alone indicate that the reason for the decrease in E_{ff} is the PC–Li reaction, as previously explained [2].
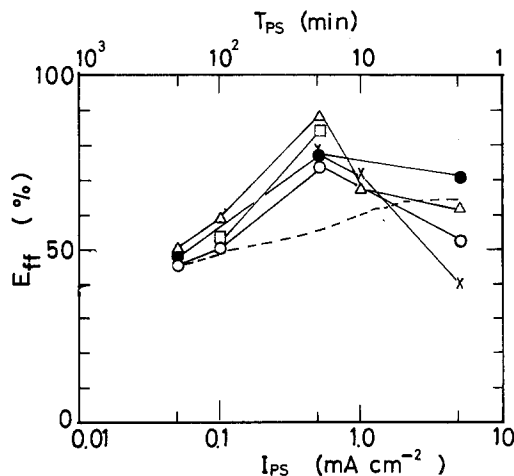
The reason for the E_{ff} maxima to I_{ps} in QID-added solutions may be explained as follows. At more than $0.5\,mA\,cm^{-2}$ the QID–Li adducts can not fully cover the deposited Li surface because of the higher deposition rate and the lack of smoothness in the deposited Li morphology. At less than $0.5\,mA\,cm^{-2}$ the gradual process of the Li–PC reaction can not be suppressed when the cycling time (T_{ps}) increases.

The morphology of the deposited Li in 1 M $LiClO_4$-PC with and without MB at $0.5\,mA\,cm^{-2}$ and $5\,mA\,cm^{-2}$ ($3.6\,C\,cm^{-2}$) is shown in Fig. 7. At $0.5\,mA\,cm^{-2}$ the morphology of the Li deposited in the solution with MB added was smoother than that in PC alone, where a dendritic Li layer was clearly observed. At a higher current density of $5\,mA\,cm^{-2}$, even with MB addition, the dendritic Li layer was observed in many places but the area of dendrites was less than for that in PC alone. These results regarding the morphology of the deposited Li agree with the results for the measurements of the dependency of Li cycling efficiency on cycling current density. Furthermore, these results support the concept that the PC–Li reaction is suppressed by the Li^+ ion conductive film formed in PC with added MB.

The $E_{ff,10}$ values in 1 M $LiClO_4$-PC with and without QID at $5\,mA\,cm^{-2}$ are summarized in Table 2. At this high current density, the $E_{ff,10}$
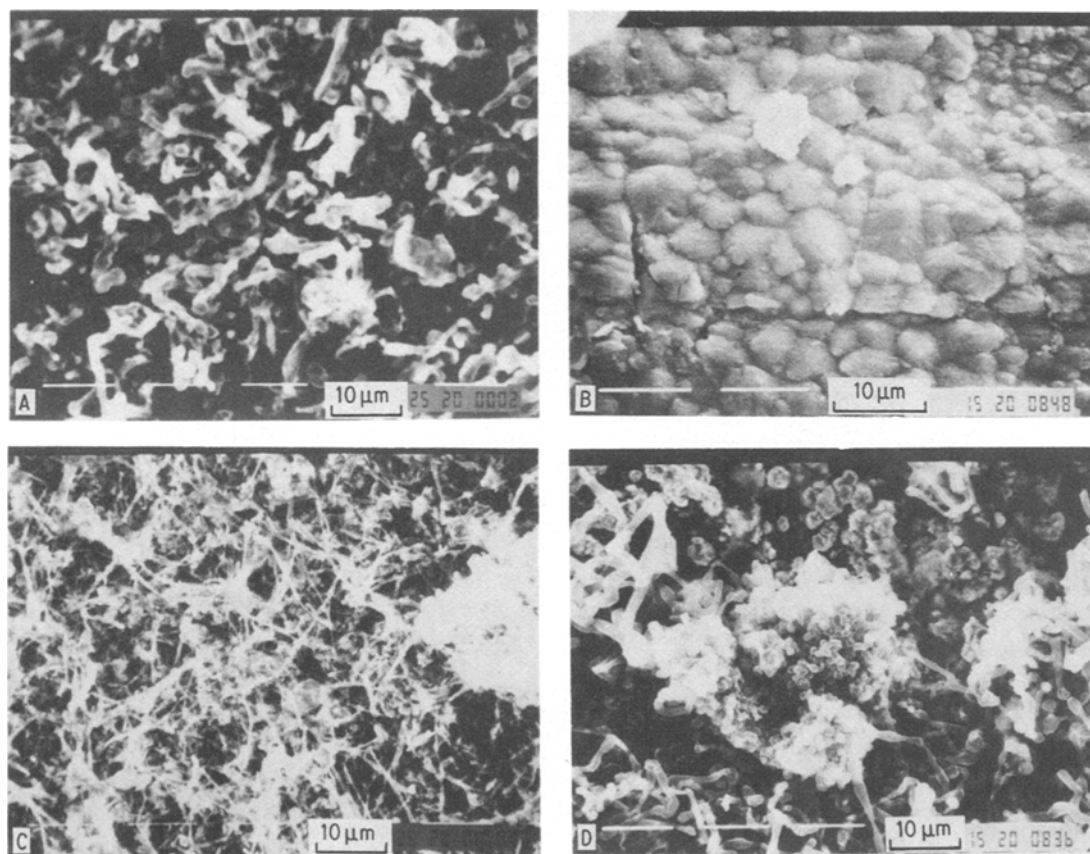
Fig. 7. Morphology for the deposited Li, $3.6\,C\,cm^{-2}$, 1 M $LiClO_4$, (A) PC, $0.5\,mA\,cm^{-2}$; (B) PC added MB ($5 \times 10^{-4}\,M$), $0.5\,mA\,cm^{-2}$; (C) PC, $5\,mA\,cm^{-2}$; (D) PC added MB ($5 \times 10^{-4}\,M$), $5\,mA\,cm^{-2}$. Scale bar: $10\,\mu m$.

values for MB and solutions with toluidine blue (TB) added were higher than in PC alone. However, additive effects were not clear for capri blue (CB) and neutral red (NR) addition.

It is considered that a QID with more reactivity to Li showed better effects on Li cycling efficiency due to the ease of formation of an Li^+ ion-conductive protection film. The difference in

Table 2. Li cycling efficiency in 1 M $LiClO_4$-PC with added QID ($10^{-3}\,M$) at $5\,mA\,cm^{-2}$, $0.6\,C\,cm^{-2}$ on the Pt working electrode

QID	$E_{ff,10}$ (%)
MB	72.1
TB	69.1
CB	27.3
NR	50.6
none	67.0

the reactivity of QID to Li can be evaluated by the reduction potential vs $Li–Li^+$. The relation between the $E_{ff,10}$ and the reduction potential (E_{red}) vs $Li–Li^+$ reported for QID [5] is shown in Fig. 8. The $E_{ff,10}$ values shown in Fig. 8 are those at $0.5\,mA\,cm^{-2}$ and $5\,mA\,cm^{-2}$. These values had a tendency to increase with the increase in E_{red} both at $0.5\,mA\,cm^{-2}$ and $5\,mA\,cm^{-2}$. The difference in the $E_{ff,10}$ between QIDs became larger at the high current density level of $5\,mA\,cm^{-2}$. These results indicate that QIDs more reactive to Li, such as MB and TB, are effective in improving Li cycling efficiency.

Conclusion

Effects of QID addition on Li cycling efficiency for $LiClO_4$-PC were examined. Through QID addition, Li cycling efficiency was improved and the morphology of the deposited Li became
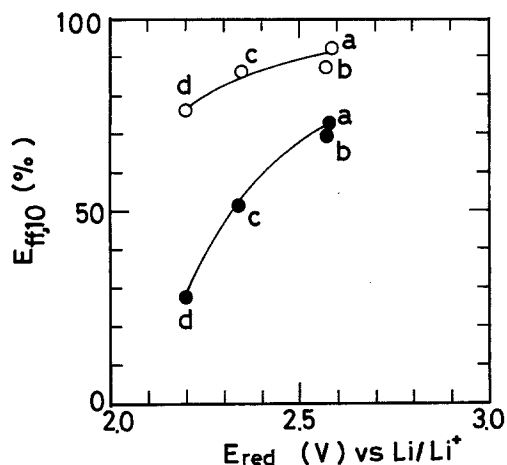
Fig. 8. Relation between average Li cycling efficiency ($E_{ff,10}$) and reduction potential (E_{red}) for QID, 1 M LiClO$_4$-PC with QID (10^{-3} M) at 0.6 C cm^{-2} on the Pt working electrode. O, 0.5 mA cm^{-2}; ●, 5 mA cm^{-2}; (a) MB; (b) TB; (c) NR; (d) CB.

smoother than that for PC. The reason for the enhancement of Li cycling efficiency in solutions with QID added seems to be due to the suppression of the PC–Li reactions by the Li$^+$ ion-conductive protective film on the deposited Li surface, as a result of the QID–Li reaction. From these results it was found to be fundamentally possible to use aromatic compounds as additives to improve Li cycling efficiency in PC, though the effects are restricted by some factors

such as current density and the amount of QID added. It is believed that aromatic compounds are prospective useful additives for the organic electrolyte systems in secondary lithium batteries.

Acknowledgements

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