Redox Shuttle Additives for Chemical Overcharge Protection in Lithium Ion Batteries

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Abstract—We disclosed that a few kinds of aromatic compounds having thianthrene derivatives with acetyl or other functional groups were stable up to about 4.2-4.3 V against lithium. These materials, called redox shuttle, have lately been employed as a chemical overcharge protection agent that consumes the excess current during battery overcharge. They oxidized above 4 V and worked as redox shuttle when introduced into the electrolyte of a Carbon/LiCoO$_2$ prismatic battery within less than one hour rate (1C). We also studied thermal properties of batteries containing the above-mentioned materials with ARC (Accelerating Rate Calorimeter). We ascertained that the current supplied over the full charge was not stored, but instantly and quite completely consumed in an oxidation-reduction reaction.

Key words: Redox Shuttle, Thianthrene Derivatives, Overcharge Protection, Oxidation-reduction, ARC (Accelerating Rate Calorimeter)

INTRODUCTION

Recently, a type of rechargeable lithium battery known as lithium-ion or rocking chair has become commercially available and represents a preferred rechargeable power source for many consumer electronics applications. Lithium ion batteries use two different intercalation compounds for the active cathode and anode materials. 3.6 V lithium ion batteries based on Carbon/LiCoO$_2$ electrochemistry are now commercially available. However, lithium ion batteries can be sensitive to certain types of abuse, particularly overcharge abuse wherein the normal operating voltage is exceeded during recharge. During overcharge, excessive lithium is extracted from the cathode with a corresponding excessive insertion or even plating of lithium at the anode. This can make both electrodes less stable thermally. Overcharging also results in heating of the battery since much of the input energy is dissipated rather than stored. The decrease in thermal stability combined with battery heating can lead to thermal runaway and fire on overcharge. Many manufacturers have decided to incorporate additional safety devices as a greater level of protection against overcharge abuse. For instance, Sony Corp. and Moli Energy Limited incorporated internal disconnect devices which activate when the internal pressure of the battery exceeds a predetermined value during overcharge abuse [Oishi et al., 1990; John et al., 1992].

These pressure-activated disconnect devices thus rely on battery constructions wherein the internal pressure is maintained below the predetermined value over a wide range of normal operating conditions, yet during overcharge the internal pressure reliably exceeds said value. Also, a net increase in internal solids volume is employed to activate a disconnect device reliably at a specified state of overcharge [David, 1990].

On the other hand, Sony disclosed the use of a small percentage of Li$_2$CO$_3$ as a cathode additive that serves as a gassing agent in

a similar manner [Yasuda, 1993]. Some aromatic compounds containing methyl groups have been used in electrolyte solvent mixtures and/or as electrolyte solvent additives in certain specific rechargeable non-aqueous lithium batteries. For instance, toluene is used as an electrolyte solvent and/or electrolyte additive to enhance cycle life [Naoyuki, 1992]. Additionally, xylene, and mesitylene are suggested for use as electrolyte additives to stop further heat generation from occurring after an internal disconnect device is activated on overcharge [Yasuda, 1992]. Thus, these additives are not employed for purposes of generating gas. However, it is speculated that methane is produced as a result of oxidation of the toluene at the voltages experienced during overcharge. Additionally, some aromatic heterocyclic compounds have been used as electrolyte solvent additives for purposes of enhancing cycle life in certain specific rechargeable non-aqueous lithium batteries. Another test cell employing an electrolyte comprising a furan solvent additive demonstrated an improved cycling efficiency for plated lithium metal [Shinichi et al., 1986]. A polyacetylene anode, TiS$_2$ cathode battery employing an electrolyte comprising a thiophene solvent additive showed better cycling characteristics than similar batteries without the additive [Masao et al., 1986]. Recently, Tadiran disclosed a method for protecting non-aqueous rechargeable lithium batteries against both overcharge and over-temperature abuse via use of a polymerizing electrolyte [Prnia et al., 1996]. The liquid electrolyte polymerizes at battery voltages greater than the maximum operating voltage or maximum operating temperature of the battery, thereby increasing the internal resistance of the battery and protecting the battery. The method is suitable for lithium batteries employing pure lithium metal, lithium alloy, and/or lithium insertion compound anodes.

It is known that certain aromatic compounds, including heterocyclic compounds, can be polymerized electrochemically [Masao et al., 1986; Prnia et al., 1996]. Waltman also disclosed the use of polymerizable aromatic monomer additives for purposes of protecting a rechargeable lithium battery during overcharge. During overcharge abuse, the aromatic additive polymerizes at voltages

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greater than the maximum operating voltage of the battery, thereby increasing its internal resistance sufficiently for protection. On the other hand, there have been several reports on chemical prevention of the overcharge of Li/TiS₂ and Li/MnO₂ lithium rechargeable batteries [Abraham et al., 1990; Narayanan et al., 1991; Golovin et al., 1992]. The redox shuttle can offer a quite good approach to cell overcharge protection. In this scheme, a material with an appropriate oxidation potential is dissolved in the electrolyte where it remains unreactive until the cell is charged fully. At a potential slightly above the cell charge limit (upper cutoff voltage), the redox shuttle is activated by its electrochemical conversion. The cell potential during overcharge is fixed at the oxidation potential of the redox shuttle. This process is supported by diffusion of the oxidized products to the anode where they recombine to form the starting material. Once the reformed material diffuses back to the cathode, it is oxidized and the cathode potential is maintained indefinitely at the oxidation potential of the redox reagent, until the time that charging is terminated.

EXPERIMENTAL

All the electrolyte solvents and salts were battery grade and were obtained from Mitsubishi Chemical Co. and Jeil Chemical Industry, respectively. The electrolyte used consisted of 1.0M-LiPF₆ dissolved in a mixture of EC (Ethylene Carbonate), PC (Propylene Carbonate), EMC (Ethyl Methyl Carbonate), DMC (Dimethyl Carbonate) with volume ratio of 35/10/35/20 in the sequential order. This formulation ratio was already determined by showing highest ionic conductivity using the Solartron Impedance Analyzer 1287/1260 model.

All reagents in solid state were obtained from Aldrich and opened in Dry Box in Argon atmosphere, then dried in vacuum oven for 2 days. Other liquid reagents were used after drying by 4A molecular sieves. The water content was measured by using the Karl Fisher 737 Titrator (Swiss Methrom Co.).

Each reagent synthesized was dissolved into the electrolyte as 50-100 mM. Cyclic voltammetry by a three-electrode cell was performed with a Solartron electrochemical interface-impedance/gain phase analyzer SI1287-1260 system. A 1.2 mm diam. Pt wire was used as the working electrode, a Pt plate as the counter electrode, and lithium pressed on a Ni Exmet plate was used as a reference electrode.

The potentials are shown in reference to the Lithium vs. Li⁺/Li as a matter of convenience. The first screening test was done by scanning the voltage to the cathodic direction from the rest potential to 0.2 V. For the reagents that showed no reaction here, voltage scanning was done starting from the anodic direction at 10 mV/s in the range of 3.5 to 4.5 V or 5.0 V.

After confirming the stability of the reagents by cyclic voltammetry, a charge-discharge test was performed by adding the reagents to the electrolyte in a prismatic battery. A mixture of LiCoO₂/graphite/PVdF (gravimetric ratio 90/7/3) in N-methyl pyrolidone (NMP) solvent was cast on Al foil 15 μm thick by doctor blade with 100 μm gap, then dried in convection oven for 12 hrs. After drying, the electrode was pressed twice with roll press in 90 N/cm² to make the cathode.

A mixture of nongraphitizable carbon/PVdF (gravimetric ratio

93/7) in NMP was cast on copper foil 19 μm thick by same method as cathode, then finally pressed with roll press machine.

The battery was charged and discharged according to the respective test condition, but the usual test condition is as follows: to begin with, charge was done with constant current and constant voltage (CC/CV) mode up to 4.2 V, applying 0.5 hour rate (0.5C), 1 hour rate (1C). On the other hand, discharge was done with constant current mode up to 2.75 V, applying 0.2 hour rate (0.2C), 0.5C. 1C. The heat flow of the prismatic battery during overcharge was measured with a Thermal Hazard Technology ARC calorimeter.

1. Synthesis of Compounds

1-1. Compound (1), 2,7-diacetylthianthrene

10 g thianthrene (0.0462 mole) was dissolved in 40ml methylene chloride, then 15 g acetyl chloride (0.185 mole) was added and stirred for 10 min. Continuously, 15 g aluminum chloride (0.112 mole) was slowly added little by little over 30 min. After thianthrene was confirmed to have disappeared from solution, this solution was refluxed, and the reaction was nearly finished by slowly adding a little leftover amount of aluminum chloride. This product was poured into 100 ml iced water little by little. After organic composed layer was separated and uptaken, crude product was washed twice with 150 ml water, then once again washed with sodium hydro carbonate solution, then dried over magnesium sulfate anhydride. After this was vacuum distilled, resultant product was separated with column chromatography by using eluent solution of Ethyl acetate vs. Hexane (1 : 9 volume ratio) solution. A 2.14 g weak yellow solid pure product was obtained. Yield was 15%, and the melting temperature was 173 °C. NMR (in CDCl₃): 2.5 (s, 6H), 7.4-7.9 (m, ArH) (unit: ppm).

1-2. Compound (2), 2,7-dibromothianthrene

15 g thianthrene (0.0462 mole) was dissolved in acetyl hydroxide 70 ml, then this solution was heated into 80 °C; herein bromine 10.8 g (0.139 mole) was added and refluxed over 8 hrs. First, yellow solid was obtained by decreasing temperature from 80 °C to room temperature. Secondly, crude white solid 2.8 g was obtained by filtration and recrystallization 5 times. Yield was 25% and melting temperature was around 145 °C. NMR (in CDCl₃): 6.89 (d, 2H), 6.97 (d, 2H), 7.17 (s, 2H) (unit: ppm).

1-3. Compound(3), 2,7-diisobutanoylthianthrene

10 g thianthrene (0.0462 mole) was dissolved in 40 ml methylene chloride solution, then 20 g isobutyl chloride (0.185 mole) was added and stirred for 10 min. Then, 15 g aluminum chloride (0.112 mole) was slowly added little by little over 30 min. After thianthrene was confirmed to have disappeared from solution, this solution was refluxed, and the reaction was nearly finished by slowly adding a little leftover amount of aluminum chloride. This product was poured into 100 ml iced water little by little. After organic composed layer was separated and uptaken, crude product was washed twice with 150 ml water, then once again washed with sodium hydro carbonate solution, then dried over magnesium sulfate anhydride. After this was vacuum distilled, resultant product was separated with column chromatography by using eluent solution of Ethyl acetate vs. Hexane (1 : 9 volume ratio) solution. 1.40 g weak yellow solid pure product was obtained. Yield was 75%, and the melting temperature was 109 °C. NMR (in CDCl₃): 1.17 (d, 12H), 3.4-3.5 (m, CH), 7.2-8.0 (m, ArH) (unit: ppm).

1-4. Compound(4), 2-acetylthianthrene

10 g thianthrene (0.0462 mole) in 40 ml methylene chloride solution was dissolved, then 10 g acetyl chloride (0.128 mole) was added and stirred for 10 min. Then, 15 g aluminum chloride (0.112 mole) was slowly added little by little for 30 min. After confirming the disappearance of thianthrene in solution, then with this solution we finished the refluxing, reaction by additional adding the little remaining aluminum chloride slowly. Crude product was poured into 100 ml iced water little by little.

After the separated organic part was taken, crude product was washed twice with 150 ml water, once again washed with sodium hydro carbonate solution, then dried over magnesium sulfate anhydride. After vacuum distillation, the resultant product was separated with column chromatography by using eluent ethyl acetate vs. Hexane (1 : 9) solution. A yield of 2.47 g weak yellow solid pure product was obtained showing 23%, the melting temperature was 173 °C. NMR (in $CDCl_3$): 2.5 (s, 5H), 7.4-7.9 (m, ArH) (unit: ppm).
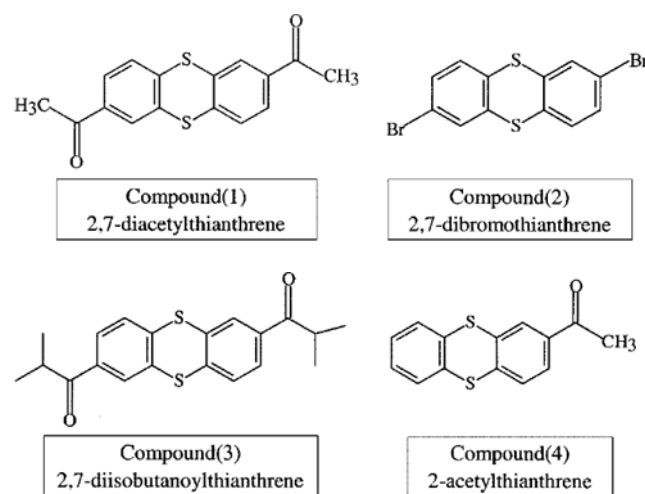
RESULTS AND DISCUSSION

1. Redox Shuttle Compounds

A covalent bond of two atoms of an organic compound, in principle, is such that two electrons forming a pair form one single bond. Therefore, when an organic compound is oxidized or reduced to remove or add one electron from an electron system of the bond of the organic compound, an unpaired electron is formed in the organic molecule compound. Although the unpaired electron can be stabilized when decomposition of the organic compound has resulted in a novel bond with another molecule being formed, the state of the organic compound having the unpaired electron is unstable in principle.

However, in the case where unpaired electrons exist on a delocalized orbit and spread over two or more atoms in a molecule as can be observed in a p-orbital of an aromatic series, the organic compound is able to relatively stably exist even if the organic compound has unpaired electrons. If the reaction active point at which the density of the unpaired electrons is high is protected from attacks of other molecules due to a steric hindrance of the substitutional group, the organic compound even having unpaired electrons is made to be more stable. Usually, acetyl and isobutanoyl groups are inducing electronwithdrawing than halogen groups, so redox potential range is a little bit higher.

Since the oxidation-reduction potential is substantially determined depending upon the degree of spread of the unpaired electrons and the symmetry of the orbit, excess spread of the orbit causes an unsatisfactory state to be realized because the oxidation-reduction potential becomes inappropriate. Compounds of the types expressed by the Fig. 1 having a basic skeleton composed of the benzene ring, which is an aromatic ring having a relatively small molecular weight, are preferred compounds to serve as the redox shuttles in view of the oxidation-reduction potential.

Since the benzene ring, which is the basic skeleton of the compound, has a molecular weight of 78, the benzene ring has smaller molecular volume as compared with metal complex type molecule, such as metallocene, polypyridine complex or cerium ions. The foregoing fact means that the volume sharing in the electrolyte is small and the dispersion rate is high. Thus, a satisfactory operation can be performed as the redox shuttle. The benzene compound has an

Fig. 1. Chemical structure of thianthrene derivatives for overcharge protection. The nomenclature for the additives are recorded in parenthesis under each structure. The numbers in parentheses correspond to the compound number in the text.

effect to serve as the redox shuttle, that is, an effect of consuming the overcharge current by the oxidation-reduction reactions. That is, it has an appropriate oxidation-reduction potential as the redox shuttle for a 4-V-class battery and is able to chemically stabilize oxidation species and reduction species by selecting a substitutional group.

2. The Introduction of Substitutional Group

The selection of the substitutional group induced into the benzene ring is performed mainly in consideration of the characteristic of the substitutional group for attracting electrons or electron donating characteristic on the basis of the oxidation-reduction potential andthe operating voltage range due to the p-electron orbital energy of the molecule. A fact about the benzene compound has been known that a substitutional group of a type attracting electrons, in many cases, raises the oxidation-reduction potential and a substitutional group of an electron donative, in many cases lowers the oxidation-reduction potential. Moreover, effects of plural substitutional groups frequently exhibit reversible characteristics.

Among the substitutional groups to be induced into the benzene compound, the alkyl group and alkoxy group are electron-donative substitutional group and mainly have the effect of adjusting the oxidation-reduction reaction potential. On the other hand, the halogen group, which is an electron-attractive substitutional group, does not considerably affect the oxidation-reduction potential but has the function of improving the stability of the performance of the battery at high temperatures.

That is, the electron-donative group of the benzene compound lowers the oxidation-reduction potential as described above and activates the electrophilic substitution reactions of the oxidizer in the system. On the other hand, the electron-abstractive group deactivates the electrophilic substitution reactions.

In order to shift the redox potential to more positive values, it is necessary to modify the thianthrene structure by replacing hydrogen atoms on the aromatic rings with electron-withdrawing groups.

The reason why the halogen group is selected as an electron-at-

tractive group for deactivating the electrophilic substitution reactions of the oxidizer is that the halogen group has a significant effect of deactivating the electrophilic substitutional reactions but a restrained effect of raising the oxidation-reduction potential. The reason for this is that the halogen group has a great resonant effect in the substitutional group. The resonant effect in the substitutional group lowers the oxidation-reduction potential because of non-localization of the molecule orbit. For this reason, thianthrene was derivatized by replacing hydrogen atoms in the 2,7-positions with diacetyl groups, according to a previously published procedure [Prema et al., 1987], diisobutanoyl groups, dibromo groups, 2-acetyl group, and further derivatized by replacing sulfur atoms with oxygen atoms. The primary purpose of the acetyl functional groups of diacetyl thianthrene is to shift the redox potential to a more positive value. In a secondary role, functional groups may be added to promote solubility of the derivatized compound in the electrolyte. Other functional groups can be attached to thianthrene to either increase or decrease its redox potential. Electron withdrawing substituents such as acetyl, bromo and diisobutanoyl groups are expected to increase the oxidation potential, while electron releasing substituents such as alkyl groups will decrease this potential. Since $LiPF_6$ or the like, which is generally employed as a support salt in the electrolyte, is a strong Lewis salt, it sometimes becomes an oxidizer having strength capable of attacking the benzene compound if the temperature is relatively high.

In a battery system having a strong Lewis acid, such as $LiPF_6$, as a support salt, the effect of the halogen group deactivates the electrophilic substitution reactions due to $LiPF_6$ at high temperatures. As a result, the stability of the benzene compound at high temperatures can be improved and deterioration in the performance of the battery taking place due to oxidation of the benzene compound can be prevented.
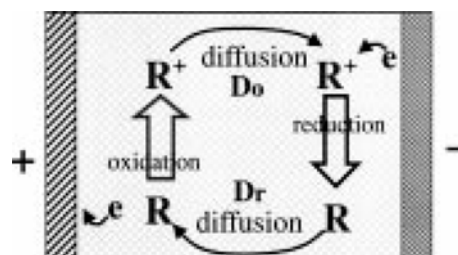
That is, the oxidation-reduction potential of the organic compound is mainly determined depending upon the basic skeleton of the molecule. The oxidation-reduction potential can be varied by hundreds of mV depending upon the type of the electrolyte for dissolving the organic compound. Therefore, the substitutional group must be selected appropriately to precisely adjust the potential.

When these compounds were tested under the same conditions as dibenzo-1,4-dioxine, the redox potential was found to have quite shifted to for oxidation and the subsequent reduction. The redox potential ranges for the dibenzo-1,4-dioxine and derivatized thianthrene compounds are given in Table 1.
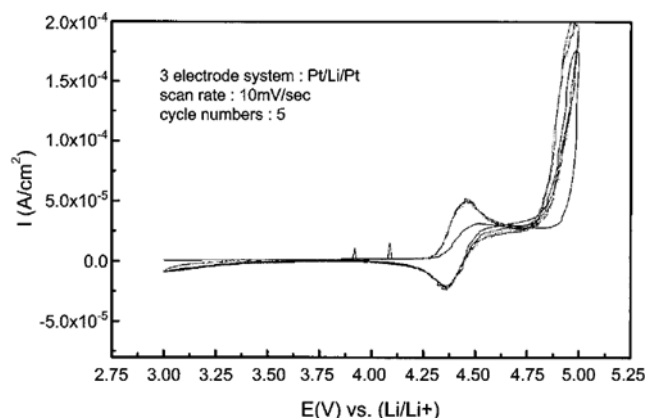
3. The Mechanism and Function

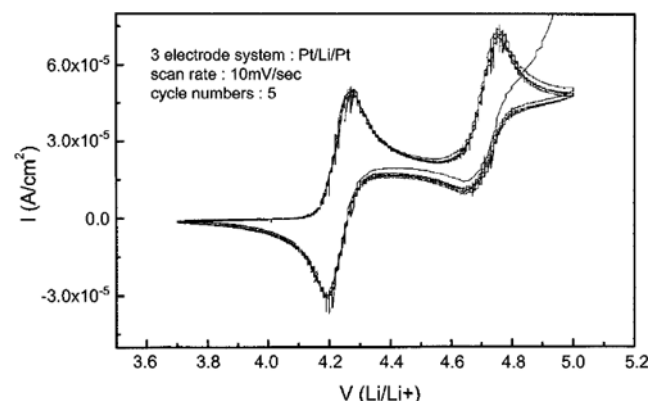The protective redox shuttle reaction is initiated when the cathode reaches the oxidation potential of the redox reagent as in Fig. 1. It proceeds with the diffusion of the oxidized species (R^+) to the anode where it is reformed. The reaction is sustained by diffusion of the reformed reagent back to the cathode. Judicious selection of the particular thianthrene will allow the overcharge protection agent to be tailored to the appropriate cell voltage. The redox potential of prospective shuttle candidates is determined readily from cyclic volt-

Fig. 2. Redox shuttle effect, in real Carbon/$LiCoO_2$ battery system, during overcharging, oxidized materials are moved by diffusion and reduced in near anode surface, and adversely reduced materials are oxidized consuming overcharge current. As a result, charge potential can be suppressed and maintained at redox shuttle potential.

Fig. 3. Cyclic voltammogram of 10 mM 2,7-dibromothianthrene in EC/PC/DMC/EMC (35/10/20/35 volume ratio%)+1.0 M-$LiPF_6$.

Fig. 4. Cyclic voltammogram of 10 mM 2,7-diisobutanoylthianthrene in EC/PC/DMC/EMC (35/10/20/35 volume ratio%)+ 1.0 M-$LiPF_6$.

Table 1. Redox potential ranges of chemical shuttle reagents

Compound	Redox potential range (V vs. Li^+/Li)	Peak separation (ΔE_p)
Thianthrene	4.01-4.10	0.09
2-acetylthianthrene	4.10-4.20	0.10
2,7-diacetylthianthrene	4.21-4.27	0.06
2,7-diisobutanoylthianthrene	4.21-4.27	0.06
2,7-dibromothianthrene	4.37-4.43	0.06

ammetry of Pt electrode in electrolyte containing the compound of interest. For example, a solution of 50 mM 2,7-diacetylthianthrene, in EC/PC/DMC/EMC (35/10/20/35 volume ratio)-1.0 M LiPF$_6$, was tested at a scan rate of 10 mV/s. Fig. 4 shows a symmetrical wave which is characteristic of a reversible reaction with the peak oxidation current at 4.27 V and the corresponding reduction (regeneration of the starting material) at 4.21 V vs. Li$^+$/Li.

The potential of the insertion into cathode determines the suitability of the protective agent. Typical redox shuttle thianthrene oxidizes at 4.1 V vs. Li$^+$/Li. Consequently, although thianthrene [Abraham et al., 1999] exhibits good redox behavior, it is not suitable for use in the Carbon/LiCoO$_2$ cell since the activation of the redox shuttle would overlap with the removal of lithium from the cathode. This would interfere with the cathode utilization so that the cell would not charge fully.

The peak width and the peak separation for a one-electron reaction can be predicted from the Nernst equation according to Eqs. (1) and (2) below:

Peak width$=\Delta^aE_{p/2}=^aE_p-^aE_{p/2}=2.20RT/nF=0.0565/n$ at 25 °C   (1)

Peak separation$=\Delta^aE_p=^aE_p-^cE_p=2.22RT/nF=0.058/n$ at 25 °C   (2)

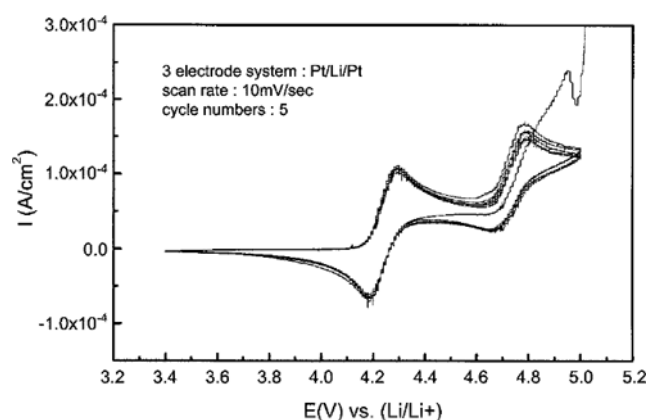The data in Table 1 were obtained from the cyclic voltammetry of

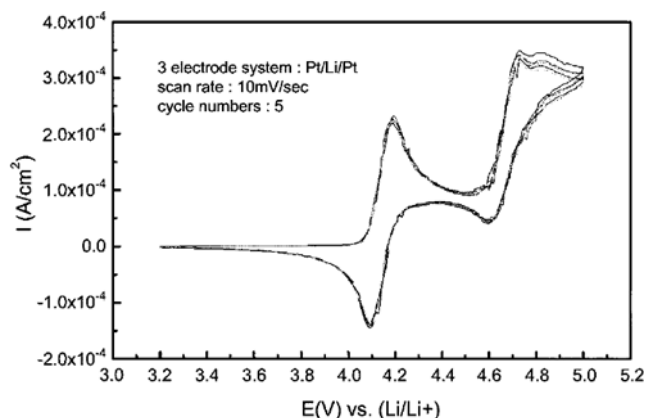Fig. 5. Cyclic voltammogram of 10 mM 2,7-diacetylthianthrene in EC/PC/DMC/EMC (35/10/20/35 volume ratio%)+1.0 M-LiPF$_6$.

Fig. 6. Cyclic voltammogram of 10 mM 2,7-acetylthianthrene in EC/PC/DMC/EMC (35/10/20/35 volume ratio%)+1.0 M-LiPF$_6$.
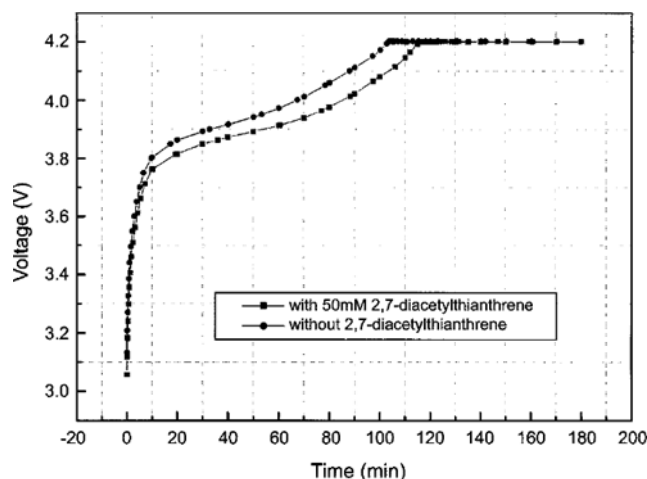

Fig. 7. Charge curves of the battery contaning without and with 50 mM of 2,7-diacetylthianthrene.

derivatized thianthrene at sweep rates of 10 mV/s, and they show close agreement between the experimental and theoretical values for peak width and peak separation exception for anthrene. This indicates that the redox of derivatized thianthrene is a reversible reaction involving a one-electron transfer. The constancy of the current function indicates that the redox reactions are diffusion controlled.

When Carbon/LiCoO$_2$ cells containing redox shuttle additives are charged under 0.5C constant current conditions, voltage profiles such as those shown in Fig. 7 are obtained. Proper matching of the overcharge protection additive (shuttle) to the electrochemical couple requires sufficient separation between the completion of lithium extraction from the cathode reaction and the onset of the shuttle activation. For this reason, an ideal match for the LiCoO$_2$ cathode would probably involve a shuttle activated at potentials between 4.2 and 4.3 V. This would ensure complete cathode utilization, yet be well within the voltage stability window of the electrolyte.

RESULTS

Cyclic voltammetry was used to screen candidates for use as redox shuttle reagents for overcharge protection in rechargeable lithium-ion battery. Results of such experiments are given in Table 1.

The requirement of the selection of a compound for use as a redox shuttle reagent for a given positive electrode is that the oxidation potential of the shuttle reagent be slightly higher than the full charge limit of the cell. The choice of a particular redox reagent will vary with the cathode material used in a rechargeable lithium-ion cell. Thus, although the carbon/LiCoO$_2$ couple is mentioned specifically, other cathodes such as LiMn$_2$O$_4$ or LiNiO$_2$ might also be used. In a lithium-ion cell with high voltage cathode such as LiCoO$_2$, oxidation of the redox reagent should take place after the full capacity of the cathode has been accessed. For LiCoO$_2$ this means that the shuttle should be activated at a potential above 4.2 V vs. Li$^+$/Li.

We have discovered that thianthrene and its derivatives such as 2,7-diacetyl thianthrene are useful as overcharge protection additives for lithium-ion battery. Substitution of acetyl groups for hy-

drogen atoms at the 2,7-positions in thianthrene resulted in a shift of the redox potential to values more positive than those obtained with thianthrene. The preferred electrolytes are resistive to oxidation in this range. In particular, liquid electrolytes with ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and similar solvents or mixtures of solvents are known to those used in the system as desirable electrolytes for use with high voltage cathodes. The same is true for these solvents or mixtures of solvents and the solvates which they form with lithium salts such as $LiAsF_6$, $LiPF_6$, $LiClO_4$, $LiN(SO_2CF_3)_2$, $LiC(SO_2CF_3)_3$, $LiBF_4$ etc.

However, since the redox shuttle actually has a limiting current, a satisfactory effect of preventing overcharge cannot be obtained if the overcharge electric current is greater than a predetermined value. Specifically, the limiting current of each of the redox shuttles, which have been suggested, is not sufficiently large with respect to overcharge occurring in a case where charge has been performed at a rate (current capacity/charge period) of 1, that is, charge has been performed with a constant current of 1C (Ah/h) or greater.

To prevent overcharge occurring with a larget current, the another method using an electronic circuit or the method of mechanically interrupting the electric current using generation of gas if overcharge takes place is relatively effective. Therefore, in a case where the redox shuttle is employed in a battery system in which charge is performed with a large electric current, another method must also be employed. But another method is beyond our current interest, so we focus only on redox shuttle additives.

The charge curves of a Carbon/LiCoO$_2$ battery with and without 2,7-diacetylthianthrene are shown in Fig. 7. As the figure shows, the voltage increase at charging was delayed, but did not level off. Even though the dependence on the concentration of the reagent was not known, 50 mM was the maximum that could be dissolved. There was no large drop of voltage after full charging nor at the beginning of discharge, suggesting that there was no internal short circuit or large resistance to cause an IR drop.

A Carbon/LiCoO$_2$ battery was again assembled, and the charge and discharge curves at overcharge were observed. The results are shown in Fig. 8. The voltage of battery with reagents showing re-
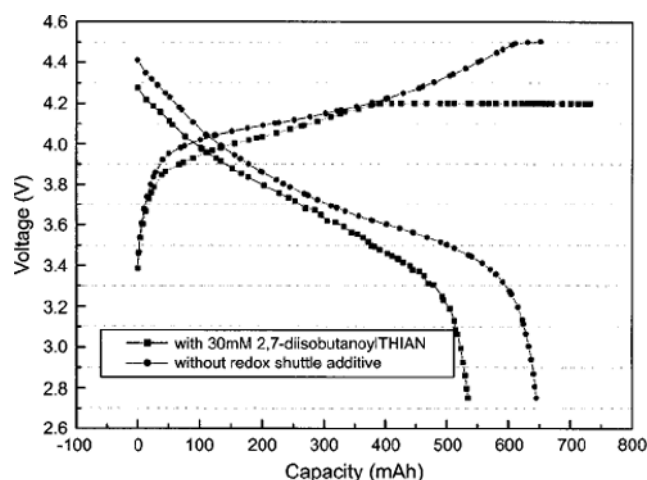
dox reactions was maintained at what we call a shuttle voltage even when overcharge current was supplied, whereas the voltage of the battery without any reagent increased up to the cutoff voltage. The same phenomenon was seen even after 4 weeks of storage. The shuttle voltage varied according to the oxidation potential of reagents; also, discharge capacity varied with the shuttle voltage.

The temperature increase and explosion of batteries with and without 2,7-diacetylthianthrene, 2,7-diisobutanoylthoanthrene and 2,7-dibromothianthrene during overcharge was measured by using a calorimeter to determine how the applied current is converted into oxidation-reduction reaction as shown in Fig. 9 and Fig. 10. Especially from Fig. 9 batteries with the above-mentioned redox shuttle additives were resistant to overcharge quite longer than batteries without them. This means that much of the current supplied over 4.2 V is not stored in the battery or consumed in a side reaction but is nearly completely converted into oxidation-reduction reaction. Until just before thermal runaway, self-sustaining reaction is con-
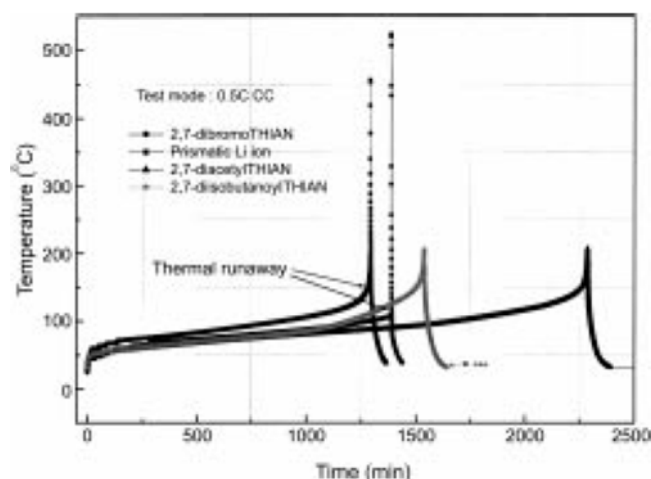
Fig. 9. ARC test of batteries of containing with and without redox shuttle additives 2,7-dibromothianthrene, 2,7-diisobutanoylthianthrene and 2,7-diacetylthianthrene respectively, where THIAN is abbreviation of thianthrene.

Fig. 8. Charge and discharge curves of the battery containing without and with 30 mM of 2,7-diisobutanoylthianthrene.
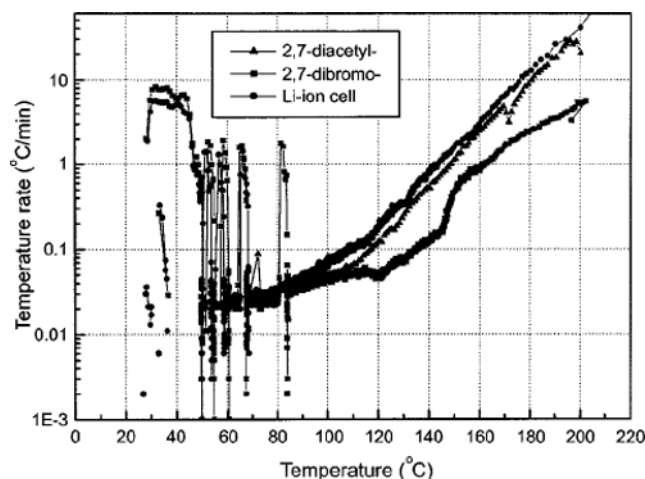
Fig. 10. ARC test of batteries containing with and without redox shuttle additives 2,7-diacetylthianthrene, 2,7-dibromothianthrene, where Li ion cell has none of additives.

Fig. 11. Swollen shape of battery just after 1C/2V overcharge ARC test.

tinuing; this means that Solid Electrolyte Interface (SEI) near to anode electrode is continuously decomposing. Thermal runaway is brought about when delithiated $LiCoO_2$ is decomposing. On the other hand, $LiMn_2O_4$ is said to be resistive to thermal decomposi-

tion at high temperature [Sun et al., 1998].

In this experiment, we charged 0.5C rate except for 1C rate, in order to see the graph in detail around thermal runaway. Generally, no work is done by the current to change the state of the battery system, and all the current supplied is consumed by the redox reaction. Fig. 10 strongly supports the above statement. Above 80 °C, there is some difference in temperature rate, which means that redox shuttle additives can surpress temperature increases. Fig. 11 shows the result of ARC test with 1C, 12 V mode. The test battery is charged fully with IC rate and then, it is once again charged fully with 1C rate for 2.5 hrs. Usually, the voltage of the battery goes up to 12 V within and around 1.5 hr after charging, then voltage is maintained at that point until end of charging. Sometimes bad batteries are fired or exploded, severely damaging electronic appliances. Even though the battery did not explode, it usually approached breakdown. Of course, the battery was not recovered any more, because most of the electrolyte was evaporated, and separation between electrode and separator occurred. Fortunately, in our case, a battery was swollen after overcharging without showing any fire or explosion. So, we can consider that the redox shuttle can also surpress 1C over-
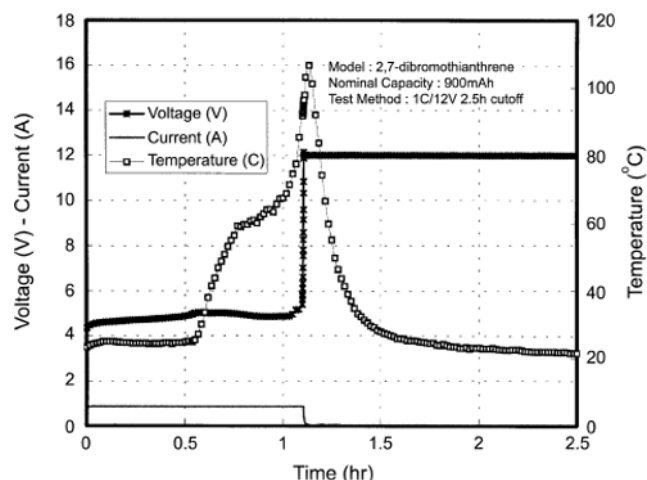

Fig. 12. ARC test result containing redox shuttle additive 2,7-dibromothianthrene at 1C overcharge characteristics.
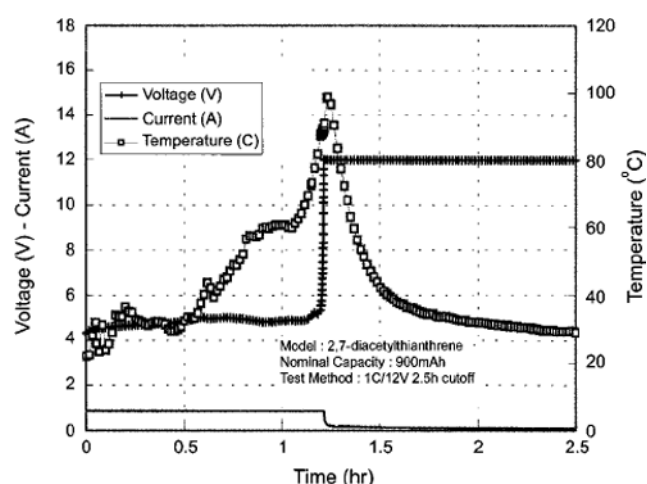

Fig. 14. ARC test result containing redox shuttle additive 2,7-diacetylthianthrene at 1C overcharge characteristics.
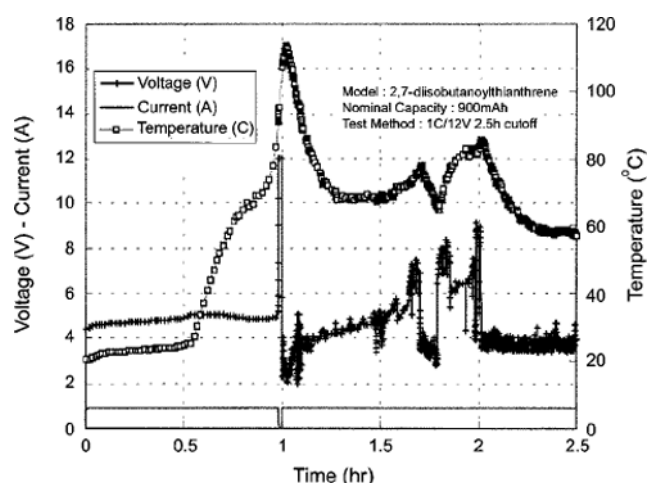

Fig. 13. ARC test result containing redox shuttle additive 2,7-diisobutanoylthianthrene at 1C overcharge characteristics.
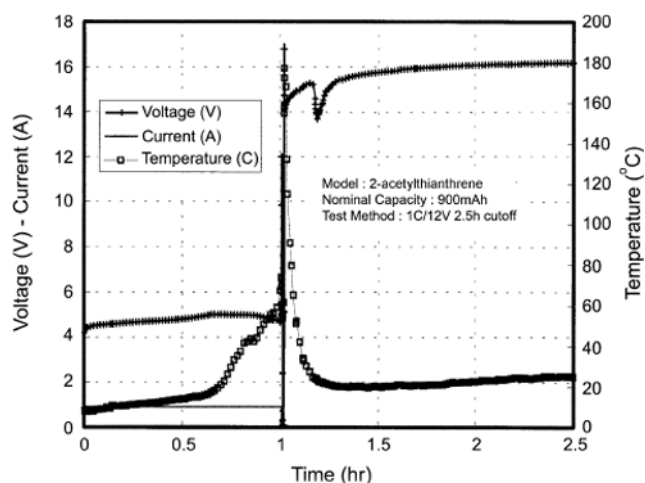

Fig. 15. ARC test result containing redox shuttle additive 2-acetylthianthrene at 1C overcharge characteristic.

charging. From Fig. 12 through Fig. 15, all of them passed 1C/12 V test. This test is a criterion for screening whether a battery can be applicable to use as a power source to many portable electronic appliances, for example, cellular phones, PDA's, and Notebook PC's etc.

In some cases, the 1C/12V test is a very severe condition, because as the capacity of the battery becomes higher, the more the battery experiences severity during overcharge. Even in the case of 2-acetylthianthrene, there is no explosion or fire, so it means that our redox shuttle additives are very powerful candidates for overcharge protection. Even though 2,7-diisobutanoylthianthrene, as in Fig. 13, shows a little bit unstable profile, at any rate it works as a redox shuttle in this overcharging test. All of batteries show common phenomena, that is, both temperature and current remarkably decreased after reaching 12V culmination. It means that batteries with our redox shuttle additives are safe and stable under 1C overcharge test. But even though we did not offer in this paper results about 2C or higher C rate, none of the batteries could pass. So, we ascertained these redox shuttle additives are suitable only within 1C or lower rate.

CONCLUSION

Thianthrene compounds with one or two alkyl groups and a halogen directly substituted on the benzene skeleton are stable up to about 4.2 V and oxidize above this potential. These compounds work as redox shuttle overcharge protection when added to the electrolyte of a Carbon/LiCoO$_2$ battery. The voltage leveled off right above the full charge voltage even when overcharge current was supplied. The current supplied over the full charge voltage was not stored in the battery or consumed in a side reaction, but nearly completely converted into oxidation-reduction reaction. Also in a certain lower rate, it could work as an overcharge protection.

NOMENCLATURE

^aE_p : anodic peak voltage
^cE_p : cathodic peak voltage
$\Delta^aE_{p/2}$: peak width
ΔE_p : peak separation
1C rate : the rate in which the capacity is consumed over one hour

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