Improvement in safety and cycle life of lithium-ion batteries by employing quercetin as an electrolyte additive

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HIGHLIGHTS

► Quercetin, an organic antioxidant, has been employed as an additive in lithium cells.
► The quercetin enhances the electrochemical performance and the overcharging tolerance of EC/EMC/DMC electrolyte.
► The quercetin-containing lithium battery shows excellent capacity retention under 1 C over 350 cycles.
► The addition of quercetin in the electrolyte shows smaller resistance than controlled one after cycling.

ARTICLE INFO

ABSTRACT

Quercetin, an organic antioxidant, has been employed as an additive in lithium-ion cells to enhance the electrochemical performance to enhance the cycle life and the overcharging characteristics of $LiPF_6$/ EC + EMC + DMC (1 M) when used as an electrolyte. A $LiCoO_2$/graphite full cell with 0.05% quercetin showed a significant improvement in safety associated with overcharging tolerance and thermal stability, without causing damage in C-rate capability, and even a small improvement in cycle life performance. The quercetin-containing lithium battery showed an improvement in its electrochemical properties with 92% capacity retention after 350 cycles from 2.8 to 4.3 V, at a rate of 1 C; compared to 85% capacity retention for a cell without quercetin operated under the same conditions. The electrochemical impedance spectroscopy (EIS) results for the $LiCoO_2$ cathode show that the addition of 0.05% quercetin provides a significant suppression in the impedance of the cell after 60 cycles. The improvement might result from the formation of a passivation microstructure (from quercetin oxidation) on the electrode's surface. The quercetin-containing batteries provided long term cycling and a high safety performance, making them a viable power source for applications involving electric devices with significant safety requirements.

1. Introduction

Lithium-ion batteries have been extensively adopted for use in consumer electronic devices, due to their high specific energy and energy density. Most commercially available rechargeable lithium-ion batteries are based on $LiCoO_2-$ or $LiMn_2O_4-$graphite electrochemistry [1–3]. One of the problems hindering the commercial application of large capacity lithium-ion batteries is the safety concern associated with them [4,5]. Explosive accidents, and fire related incidents, involving Li-ion batteries are still frequently recorded; however, most incidents appear to involve overcharging or overheating. In most cases the typical liquid electrolyte solutions used for lithium-ion batteries are organic solutions, such as ethylene carbonate (EC)-, ethyl methyl carbonate (EMC)-, di-methyl carbonate (DMC)-based solutions containing lithium salts such as $LiPF_6$, $LiClO_4$, and $LiBF_4$. However, these liquid electrolytes are easily flammable. The temperature and the internal pressure of the battery increase with an increase in internal impedance during overcharging, finally resulting in fire and explosion.

Safety is an important issue for lithium-ion batteries when they are overcharged. It is well known that the addition of 'additive packages' to electrolytes will alter their electrochemical performance. Several kinds of additives have been proposed to improve
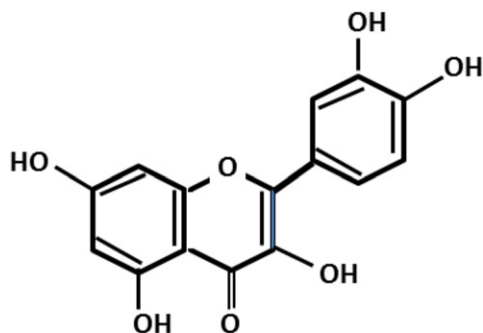
Scheme 1. Chemical structure of quercetin.

Fig. 1. Manufacture of prismatic soft pack full-size lithium-ion batteries (LIBs).

the cell's overcharging performance and flame retarding ability. The use of redox shuttle additives seems to be an effective way to improve overcharging performance [6,7]. A redox shuttle is an electrolyte additive that can be reversibly oxidized-reduced at a characteristic potential to provide an intrinsic overcharge protection for lithium-ion batteries. To improve the thermal safety and the cycling performance of lithium-ion batteries, various fire-retardant organic phosphates have been investigated, including trimethyl phosphate [5,8,9], tri-(4-methoxythphenyl) phosphate [10], and tris(2,2,2-trifluoromethyl) phosphate (TFP) [11]. Additionally, several polymerizable molecules, which form conducting [5,11,12] or isolating polymers [13] in the batteries during overcharging, have been suggested as safety additives that can bypass or interrupt the internal current flow. Interesting in this respect is tri-(4-methoxythphenyl) phosphate which provides both fire-retarding and polymerized overcharge protection. The most common explanations for the improvements afforded by these additives are: (1) the physical barrier forming process, which builds up an isolating layer on the surface of the electrode so as to stop the combustion process [9] and (2) the chemical radical-scavenging process, which terminates the radical chain reactions responsible for the combustion reaction.
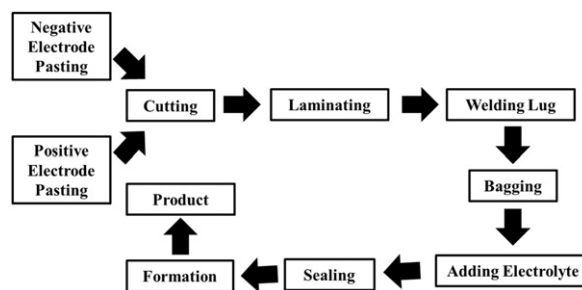
However, the improvements obtained with respect to electro-lyte safety in terms of flame retardation and overcharging pro-tecting are typically accompanied by degradation of the cell's key performance indicators such as its capacity, due to modifications in the electrolyte's diverse viscosity and ionic conductivity.

Quercetin is a polyphenolic three-ringed flavonoid compound with five phenolic hydroxyl groups that possesses antioxidant properties commonly used to protect food, pharmaceuticals and cosmetics from spoilage [14]. Its chemical structure is shown in Scheme 1. Thus, we were interested in investigating a potentially similar 'protective' role for "quercetin" as an electrolyte additive in lithium-ion cells. The aim of this study was to examine the effect of quercetin as an additive on the cell's electrochemical performance with respect to charging/discharging, impedance, cycle life and overcharging safety.

2. Experimental

To examine the electrochemical influence of quercetin as an additive, we selected 1 M LiPF$_6$ in EC/EMC/DMC (1:1:1, v/v/v) supplied by UBK Co. Ltd., China as the base electrolyte into which, in an argon-filled glove box (water content less than 10 ppm), varying amounts of quercetin were added. The positive electrode consisted of 90 wt.% LiCoO$_2$ as an active material, 8 wt.% polyvinylidene

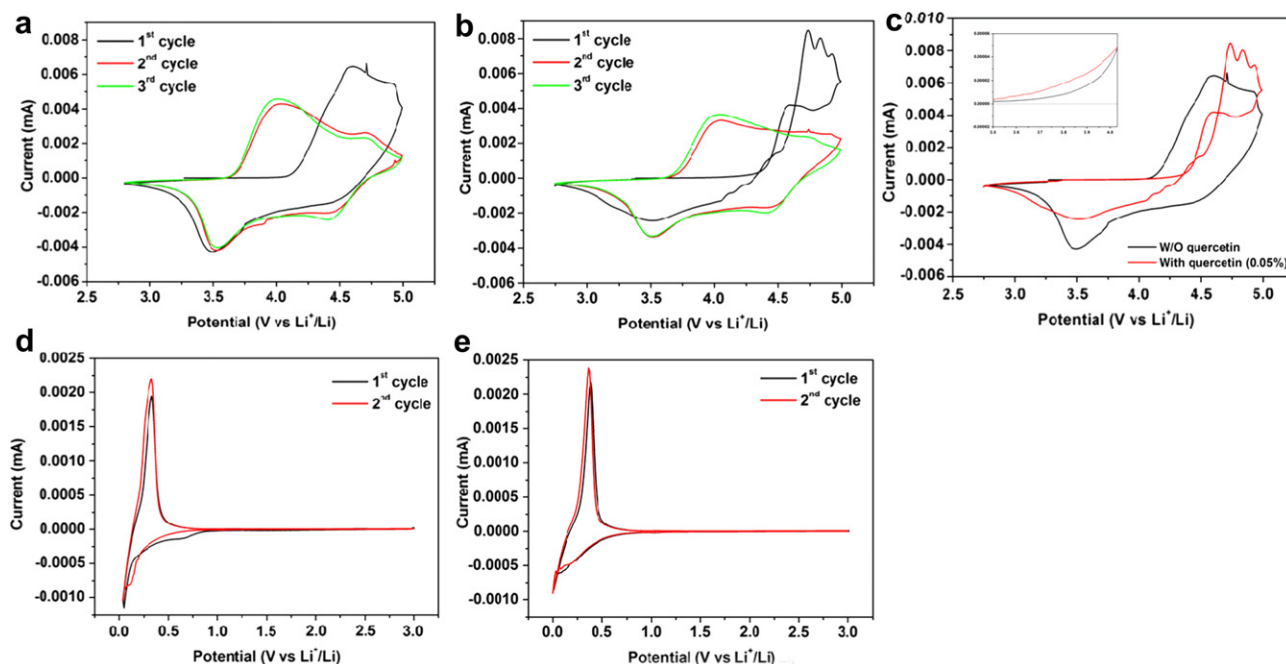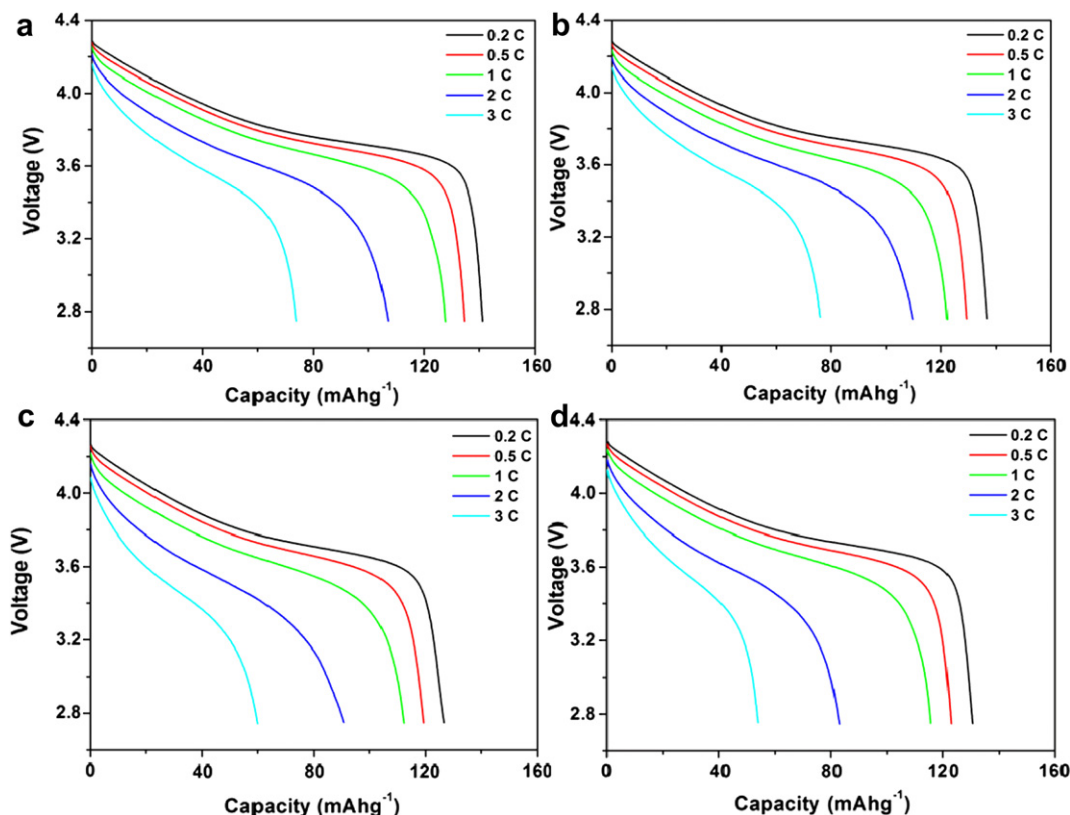**Fig. 2.** CV curves of (a) LiCoO$_2$ cathode half cell without quercetin, (b) LiCoO$_2$ cathode half cell with 0.05% quercetin, (c) the first cycle comparing in LiCoO$_2$ cathode, (d) graphite anode half cells without and (e) with 0.05% quercetin.

Fig. 3. Discharge curves with various discharge rates from $LiCoO_2$ half cells charged at C-rate of 0.2 C under CC/CV mode and with various amounts of added quercetin (a) 0%, (b) 0.05%, (c) 0.075%, and (d) 0.1%.

difluoride (PVDF) as the binder, and 2 wt.% KS4 as the conductive material. The negative electrode contained graphite (90 wt.%), PVDF (8 wt.%), and KS4 (2 wt.%). To investigate the oxidation potential of the electrolyte, cyclic voltammetry (CV) experiments were carried out using a 2032 coin-type half cell with the as-made graphite or $LiCoO_2$ electrode as the working electrode. The counter electrode of each half cell was lithium metal (potential is 0.005 V). A porous polypropylene film served to separate the cathode and anode. A coin cell (type 2032), with an electrode diameter of 1.4 cm (mass 23–25 mg), was assembled in a dry room and used for the test. The CV curves were recorded on an AutoLab Instrument. The scan rate was 0.3 mV s^{-1} in the potential range 3–0 V for the graphite half cell and 3–5 V for the $LiCoO_2$ half cell.

Working electrode Galvanostatic charge–discharge measurements were carried out using coin-type cells. The electrochemical properties of the cell were tested with a multi-channel automatic battery cycler (Arbin) with a constant discharging current from 0.2 C to 3 C. In the rate performance tests, the cells were charged to 4.3 V with a constant current and constant voltage (CC/CV) at a rate

of 0.2 C and then discharged to 2.75 V. In the charge/discharge cycling test, the cell was charged and discharged at the same rate repeatedly. The cut-off voltages were set at 4.3 V and 2.75 V.

AC impedance measurements of the cells were conducted using an electrochemical measurement unit (Solartron Instruments, SI1280B) under the open circuit voltage conditions also with a coin-type cell. The frequency range and voltage amplitude were set from 100 kHz to 0.01 Hz and at 5 mV, respectively, with 'Code Z-View

Table 1
Effect of discharge rate on the charge–discharge efficiency of the lithium-ion cells containing different electrolytes.

Current rate	Charge–discharge efficiency (%)			
	0% additive	0.05% additive	0.075% additive	0.1% additive
0.2 C	95.7	95.0	94.3	93.8
0.5 C	94.3	93.7	92.3	92.7
1 C	94.1	93.7	92.5	92.9
2 C	83.0	89.1	79.8	70.8
3 C	65.5	68.7	61.5	57.7
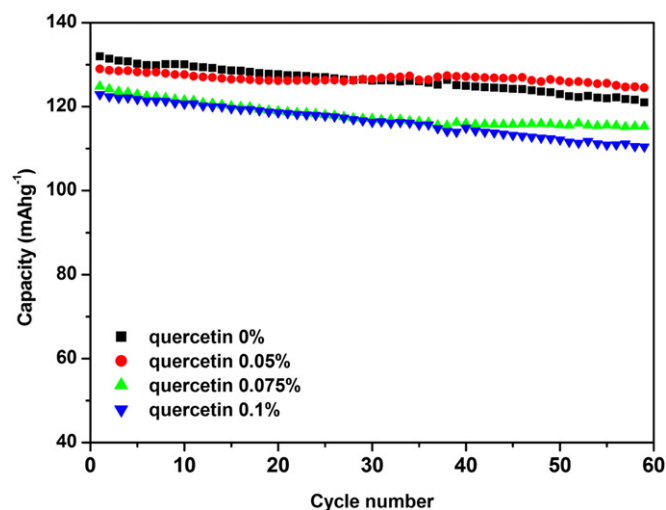
Fig. 4. Cycle life test of the $LiCoO_2$ half cells with various contents of quercetin. The cells were charged and discharged at C-rates of 0.5 C.
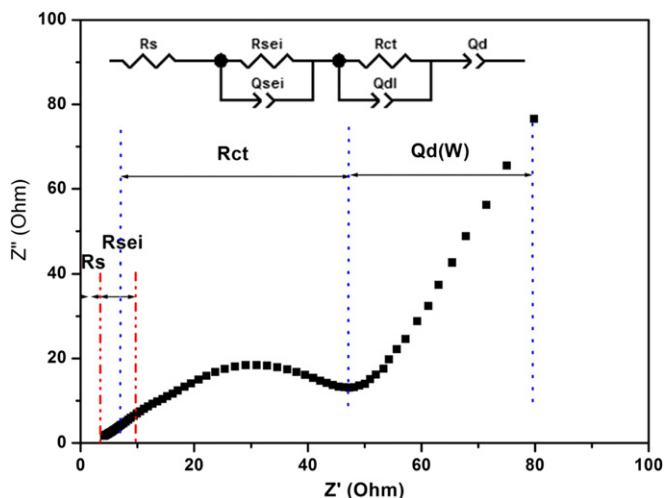
Fig. 5. The electrochemical impedance spectroscopy (EIS) measurement and the equivalent circuit of the cathode half cell.

software' being used to fit the spectra to the possible equivalent circuit.

A prismatic soft-packed lithium-ion battery (1100 mAh), which is normally 4.8 mm thick, 35 mm wide and 60 mm long (Model 483560), was assembled using a $LiCoO_2$ cathode, graphite anode and polyethylene separator. Both positive and negative electrodes were prepared using a slurry-pasting process. Quercetin (0.05%) was added directly to the 1 M $LiPF_6$ in EC/EMC/DMC.

Overcharge tests were carried out at room temperature with a soft-packed lithium-ion battery (LIB) made by the process shown in Fig. 1. The batteries were already fully charged to the cut-off voltage, i.e. at their 100% state of charge (SOC). The batteries were overcharged at a rate of 3 C to 6 V followed by a constant voltage at 6 V until the packing of the battery vented. The voltage and temperature variation were recorded during the process.

3. Results and discussion

Fig. 2(a) and (b) shows CVs of the $LiCoO_2$ electrode in a $LiPF_6$ (1 M) electrolyte, also comprising EC/EMC/DMC (1:1:1, v/v/v), with and without 0.1 wt.% quercetin. In the presence of quercetin, the oxidation current arose at a positive potential of 4.3 V (vs. Li/Li^+) in the first scanning cycle. The oxidation potential of the quercetin-containing electrolyte is a little higher than that of the electrolyte without quercetin. It shows a very different current curve in the presence and absence of the quercetin during the first cycle. Since the working voltage range of lithium-ion batteries is 2.75–4.3 V (vs. Li/Li^+), the results suggest that quercetin can be used as an additive in the lithium-ion cell electrolytes without being oxidized at their normal working voltage. The data demonstrates that quercetin as an electrolyte additive does have a remarkable effect on the electrochemical performance of the $LiCoO_2$ electrode. Fig. 2(c) compares the onset potential of the cell with quercetin added being postponed to 4.4 V, compared to that of a sample without additive which is 4.1 V. However, the curve shows a larger current response in the range 3.5–4.0 V in the quercetin added cell compared to the blank one, indicating a small amount of reaction occurs at low voltage range in the quercetin-containing electrolyte before the main peaks at higher voltage. The micro reaction could lead to an ultrathin layer which may act as a passivation film. Quercetin shows remarkable oxidation peaks in the potential region of 4.6–4.8 V in the first anodic scan and there are no obvious

corresponding oxidation peaks caused by the additive in the second scan, suggesting that an irreversible passivated interface has already formed on the cathode surface. The oxidation peaks of the polyphenolic compound, quercetin could correspond to the patterns of several benzene derivatives electrolyte additives including toluene and xylene [15]. Fig. 2(d) and (e) is the CV curves of the graphite electrode in the bare electrolyte with and without 0.1 wt.% quercetin added. For the electrolyte without quercetin, the oxidation peak observed near 0.2 V in the first cycle agrees with the common carbon or graphite electrodes [16]. A small reduction peak showed at about 0.7 V that disappeared in the second scan may be ascribed to the decomposition of the electrolyte solvent. For the graphite electrode in the electrolyte with 0.1 wt.% quercetin, the CV curves and the redox peaks seem to be similar to the electrode in the electrolyte without quercetin. They also show high uniformity in the first and second scans, indicating that the lithium ion could effectively intercalate into, and de-intercalate from, the graphite without any adverse effects. The results suggest that the quercetin supplemented electrolyte has more influence on the positive $LiCoO_2$ electrode than on the negative graphite electrode.

Fig. 3 shows the rate performance of the $LiCoO_2$ containing half cells with different concentrations of quercetin augmented electrolytes at different discharge rates, i.e.: 0.2 C, 0.5 C, 1 C, 2 C and 3 C. All of the cells were charged with the CC/CV protocol at a rate of 0.2 C under CC/CV mode. Thus the capacity decreased with an increasing discharge C-rate may be explained in terms of the electric polarization due to the increased IR drop. As demonstrated in Fig. 3(a) and (b), the cell containing 0.05 wt.% quercetin electrolyte shows a similar performance to the cell without quercetin at rates of 0.2 C to 3 C. The capacities of cells that are without quercetin and those with 0.05 wt.% quercetin added have respective discharge capacities of 141.7 and 140.2 mAh g^{-1} at the rate of 0.2 C, while their capacities at 3 C are 77.3 and 79.1 mAh g^{-1}. Fig. 3(c) shows that the discharging capacity of cells with an added 0.075 wt.% of the quercetin-containing electrolyte is 127.1 mAh g^{-1}, 111.2 mAh g^{-1}, 92.3 mAh g^{-1} and 60.0 mAh g^{-1} at 0.2, 1, 2 and 3 C-rates, respectively. However, the cell with the electrolyte containing 0.1 wt.% of quercetin exhibits analogical capacities with the one containing 0.075 wt.% at a low C-rate (<1 C), but shows poor capacities i.e. 81.5 and 53.2 mAh g^{-1} at 2 C and 3 C respectively as shown in Fig. 3(d). The efficiency of the cell is decreased with an increase in the content of additive at the same discharge rate. The decrease in the efficiency with the additive content is insignificant at the lower rate but becomes serious at higher rate, as shown in Table 1. It indicates that the additive might play a more important role at the higher rate or at the conditions with higher polarization. Fig. 4 shows the capacity retention during cycling of the $LiCoO_2$ lithium-ion half cells. The cells were cycled between 2.75 and 4.3 V at a constant current of 0.5 C. The cells with electrolyte containing 0, 0.05, 0.075, and 0.1 wt.% quercetin show capacity retentions of about 92, 97, 92, and 90% of the initial capacity after 60 cycles. In addition, their final discharge capacities are 121.0, 124.5, 115.3, and 110.4 mAh g^{-1} after 60 cycles, respectively. The electrochemical properties suggest that a quercetin content of 0.05 wt.% in $LiPF_6$ (1 M)/EC:EMC:DEC (1:1:1 by vol.%) electrolyte might be the optimum condition for improved cycling performance.

The AC impedance of the $LiCoO_2$ half cells with and without quercetin was measured in the first, the 40th, and the 60th cycles. A typical equivalent circuit used to fit the electrochemical impedance spectroscopy (EIS) curve is shown in Fig. 5. The resistance measured at very high frequencies corresponds to the resistance of the ionic electrolyte R_s and is added in series to the circuit. The resistance (R_{sei}) and capacitance of SEI layer in the high frequency semicircle are related to Li^+ migration through the SEI layer. The capacitance of SEI film is represented by a constant phase element (CPE), Q_{sei}.
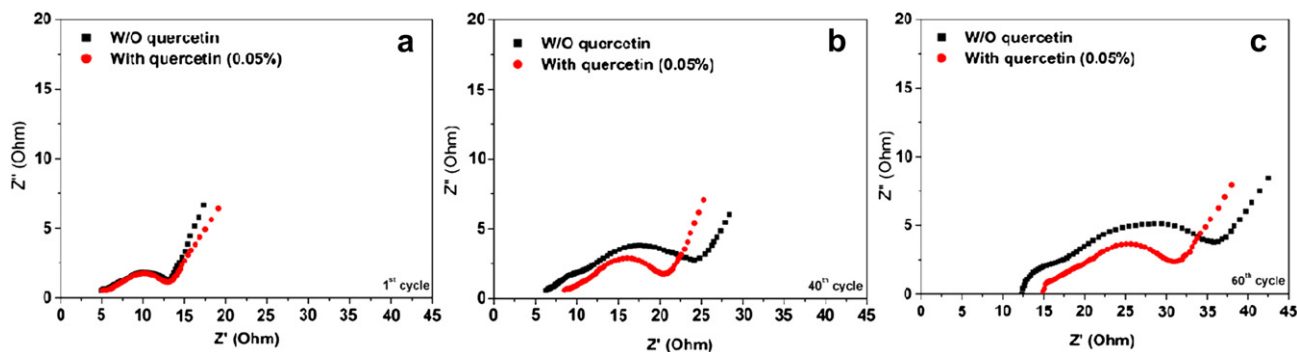
Fig. 6. Nyquist plots of the cells with and without quercetin at (a) the 1st, (b) the 40th and (c) the 60th cycles.

Table 2
Impedance evolution of the lithium-ion cells with different cycle numbers.

Cycle number	Resistance (Ω cm^2)							
	Quercetin-free				0.05 wt.% quercetin			
	R_s	R_{sei}	R_{ct}	R_{cell}	R_s	R_{sei}	R_{ct}	R_{cell}
1	5.9	4.3	6.6	16.8	5.9	4.5	6.6	17.0
40	6.3	7.0	20.0	33.3	8.2	5.1	11.3	24.6
60	12.4	8.3	28.1	48.8	14.9	7.1	15.1	37.1

The medium frequency semicircle is related to the charge-transfer resistance (R_{ct}) and capacitance of the double layer (Q_{dl}) on the particle surface [17–19]. A CPE (Q_d) in the low frequency region was chosen to represent the bulk diffusion of lithium ions. This approach, which has been used to characterize the LiM$_x$O$_y$ (M = transition metals) and other active electrode materials, yielded a good agreement with the experimental data [3,20].

Fig. 6 shows the Nyquist plots of the cells in the charged state (4 V) in the first, the 40th, and the 60th cycles of the charging–discharging processes. The corresponding impedance values of lithium-ion cells with the electrolyte with and without quercetin during cycling are listed in Table 2. In the first cycle, the R_s, R_{ct} and the total resistance R_{cell} of the cell without quercetin and the quercetin-contained cell are nearly same, indicating ionic conductivity of the cell with quercetin to be as high as the cell

without quercetin during the first formation cycle. After 40 cycles, the values of R_{sei}, R_{ct} and the total resistance R_{cell} of the quercetin-containing cell are lower than those of the cell without quercetin. A higher R_s value in the quercetin-contained cell than in the one without quercetin could be explained as an 'ingredient change of the electrolyte'. In the 60th cycle, the R_{cell} of the cell without quercetin increased 3 times to 48.8 Ω while that of the cell with quercetin increased only to 37.1 Ω. The R_{ct} of the cell without quercetin increased drastically during cycling while there was only a slight increase in the impedance for the quercetin-contained cell, this quercetin addition appears to significantly suppress the growth of the R_{ct}. It is known that the total resistance (R_{cell}) of the lithium-ion cell is mainly composed of the bulk resistance of lithium ions to diffusion, solid electrolyte interface resistance (R_{sei}) and charge-transfer resistance (R_{ct}) [21]. As indicated in Table 2, the charge-transfer resistance (R_{ct}) of the cells shows a larger increase with an increasing cycle number compared with R_s and R_{sei}. In other words, the cell impedance increasing is mainly caused by the increment of charge-transfer resistance. The EIS results suggest that the addition of 0.05 wt.% of quercetin significantly suppresses the increase in the charge-transfer resistance during prolonged cycling, thus improving the electrochemical performance of a lithium cell. The passivation film induced by the reaction with quercetin was formed on the electrode's surface and led to a better cycle life performance by suppressing the increase of the cell's impedance.

To evaluate more fully the practical utility of quercetin, LiCoO$_2$/graphite full cells were also evaluated. Fig. 7 summarizes the charge–discharge curves of the LiCoO$_2$–graphite full-size lithium battery at various current densities (indicated as C-rate). The theoretical capacity of the battery is designed as 1100 mAh, which is based on the nominal capacity of the positive electrode (LiCoO$_2$ = 140 mAh g^{-1}). At the rate of 0.5 C (550 mA), the discharge capacity of the battery without quercetin in the electrolyte (1 M LiPF$_6$/EC:EMC:DEC, 1:1:1 by vol.%) is 1196 mAh. The capacity of the battery with the quercetin-contained electrolyte is 1177 mAh at 0.5 C, which shows small difference with the electrolyte without quercetin. At a rate of 1 C (1100 mA), specific capacities of 1068 mAh and 1033 mAh are obtained in the quercetin-contained battery and the battery without quercetin, respectively. The battery with electrolyte containing 0.05% quercetin shows less serious capacity fading than a battery without quercetin in the electrolyte. The results indicate that the electrolyte additive did not change the electrochemical properties of the battery, but rather supported capacity stability during high current discharge rates. The voltage values of the 50% discharging depth in the batteries exceed 3.7 V under 0.5 C and 1 C discharging, indicating a perfect electrochemical performance.
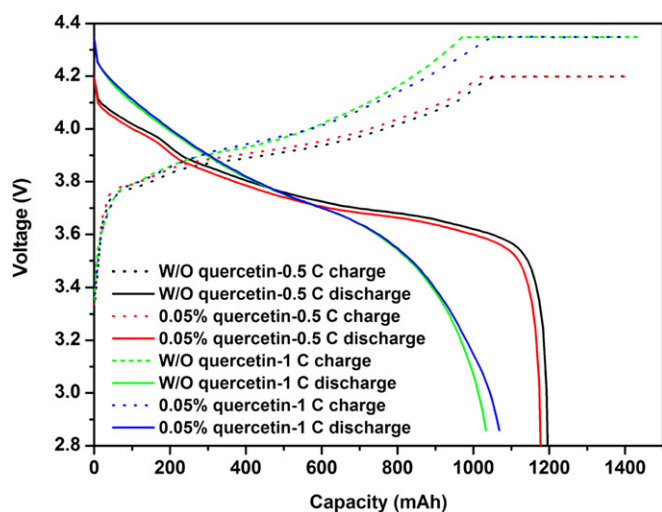

Fig. 7. C-rate performance of LiCoO$_2$/graphite LIB with and without 0.05% quercetin in electrolyte.

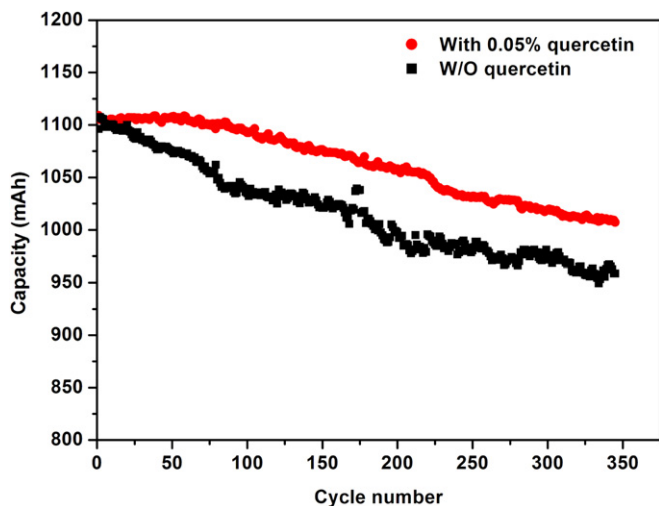**Fig. 8.** Cycle life test on LiCoO₂/graphite LIB with and without quercetin.

Fig. 8 illustrates the cycling performance of the LiCoO$_2$/graphite full-size lithium battery with a nominal capacity of 1100 mAh at a rate of 1 C between 2.8 and 4.3 V. It is clear that the battery with electrolyte containing 0.05% quercetin exhibits a better cycle life performance, compared with the battery without quercetin in the electrolyte. Compared with the capacity of the first cycle, the capacity retention of the battery with quercetin is 92% after 350 cycles, higher than that without quercetin (85%). The quercetin-containing battery also shows an improved cycling stability during the prolonged cycling process. The results also indicate that a certain amount of quercetin is compatible with LiCoO$_2$/graphite LIBs.

To examine the overcharge behavior of quercetin when used as an additive, parallel overcharging tests were performed on prismatic soft pack LiCoO$_2$–graphite batteries (Model 483560) filled with 1 M LiPF$_6$/EC:EMC:DEC (1:1:1 by vol.%) electrolyte containing

0.05% quercetin. The test battery was first cycled at 0.2 C between 2.75 V and 4.2 V for two times and then charged under 1 C to 4.2 V. The battery was almost at its 100% SOC before the test. Fig. 9(a) shows the result of overcharge tests with the 3C-6V overcharge mode. In Fig. 9(a), the voltage profiles for the batteries, with or without the addition of the additive, are similar before overcharging at 4.8 V. However, when the battery is subjected to a higher overcharging voltage, the charging curves for the two types of batteries are very different. The voltage of the battery without additive steadily increases to 5.4 V, whereas the voltage of the battery with additive increases rather gradually to 5.2 V and thereafter shows a small decrease. In the overcharging test the battery without quercetin in the electrolyte vented at 1200 s, while the battery with additive vented at 2000 s, indicating an obvious overcharge tolerance created by the addition of quercetin. The overcharging behavior could result from oxidation reactions of the electrolytes and the additive at the cathodic surface, which has been previously studied in some benzene derivatives [15]. Fig. 9(b) shows the variation of the temperature of 483560-1100 mAh batteries with healing time 1200 s after the beginning of overcharging test, the surface temperature of the battery without quercetin started to rise dramatically at about 80 °C. Conversely, this only happens to the battery containing 0.05% quercetin with 2000 s overcharging. This suggests that the quercetin may improve the safety of the Li-ion battery by supporting its thermal stability in the high potential range.

Generally speaking, cycling performance deterioration is attributed to (1) electrolyte decomposition, or the structure instability of the LiCoO$_2$ electrode and (2) the formation of a surface film on the surface of the LiCoO$_2$ particles which isolates their electronic pathways from the current collector [22]. The LiCoO$_2$ cathode reacts with a normal electrolyte to form a solid electrolyte interface (SEI) which generally leads to capacity loss decreasing electronic conductivity at about 4.2 V. It might be presumed that the quercetin participates in the electrolyte reaction by the oxidation of phenolic groups during SEI formation, thereby creating a more stable interface microstructure. This special SEI acts as a stable passivation
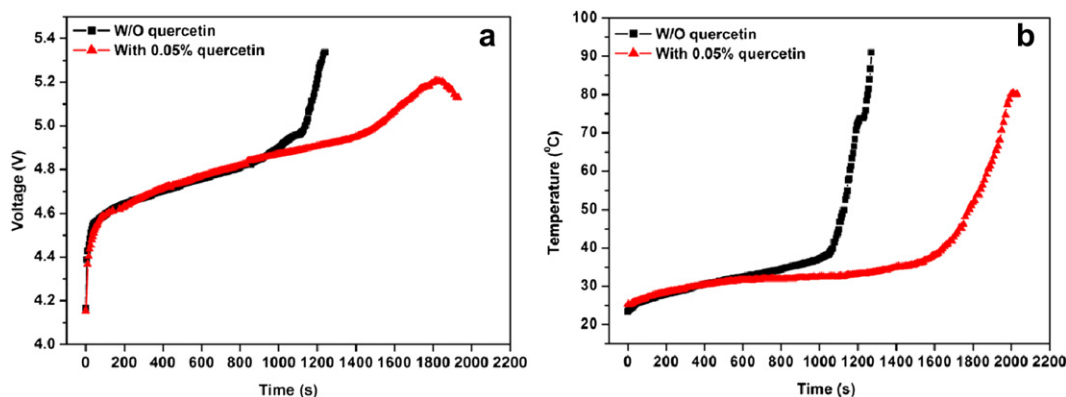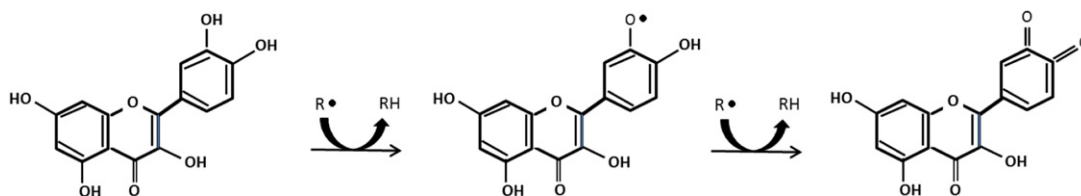

Fig. 9. (a) The overcharge curves and (b) the variation of surface temperature of LiCoO₂/graphite Li-ion batteries.

Scheme 2. Scavenging of reactive oxygen species (R•) by quercetin [23].

film to hinder the charge-transfer resistance (R_{ct}) increase during the battery cycle. The superior cycle life and anti-overcharging performance of the cell are in good agreement with the impedance spectroscopy (IS) tests.

Electrolyte additives for lithium-ion batteries generally pass through a rather complicated analysis procedure and consequently retail at a very high cost. Some incompatibility problems need to be taken into consideration before using such additives. By way of contrast, quercetin is a non-toxic material that is easily obtained at low cost, which can suppress the resistance-increase during cycling, and results in improving the safety of the lithium-ion battery without either diminishing the capacity and cycling ability. What is more, as it is well known that quercetin has a high oxygen radical absorbance capacity (ORAC) value due to its polyphenolic groups, as shown in Scheme 2, but it is unclear that the observed results are due solely to the flavonoid's antioxidant potential or to its structure. Therefore, better understanding for the enhancement in the electrochemical properties of a battery cell with various high ORAC natural antioxidants e.g. epigallogatechin, isoflavones and anthocyanidins may require further investigation.

4. Conclusion

In summary, both the safety and the cycle life of the lithium-ion batteries were significantly improved by using quercetin, an organic flavonoid compound, which is a polyphenolic antioxidant used in comestibles, as an electrolyte additive. Quercetin (0.05%) containing electrolytes exhibited better cycling ability than did the electrolytes without quercetin. The enhanced cycling performance is attributed to the impedance suppression capability of quercetin during prolonged cycles of charging–discharging. The electrolyte with quercetin exhibits overcharge tolerance and thermal stability while the lithium-ion battery undergoes overcharging, thus increasing the safety of batteries by minimizing the risk of fire and explosion. The enhanced performance of the quercetin-contained electrolyte could be due to the thin passivation microstructure on the cathode's surface formed by the polyphenolic compound which leads to the internal impedance suppression during cycling. Quercetin, already known to have a protective function as an antioxidant in physiological systems, could become a highly promising candidate as an electrolyte additive conferring similar protection to rechargeable lithium-ion batteries.

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