RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

ARTICLE

Tertiary butyl hydroquinone as a novel additive for SEI film formation in lithium-ion batteries

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Jia-Qi liu,[a,†] Quan-Chao Zhuang,[a,†] Yue-Li Shi,[a,b*] Xiaodong Yan,[b] Xing Zhao,[a] Xiaobo Chen[b,*]

Electrolyte additives play a key role in the performance of the lithium ion batteries. In this study, we reported tertiary butyl hydroquinone (TBHQ) as a new electrolyte additive with a promising prospect. It largely improved the electrochemical performance of the graphite electrode such as cyclic stability and reversible capacity. The improvement was benefited from the effective formation of a stable and compact thin solid-electrolyte-interface(SEI) film to reduce the resistance. Thus, this study demonstrated a promising electrolyte additive for improving lithium-ion battery performance.

Introduction

Currently, graphite is the most widely used anode material in commercially available lithium-ion batteries due to its relatively high theoretical capacity (372 mAh g^{-1}), low potential, moderate cost and environmental benignity.[1] $LiPF_6$-containing mixture solvents of organic carbonates are commonly used as electrolytes for lithium-ion batteries, where organic carbonates generally include ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), and ethylmethyl carbonate (EMC). It is generally known that during the first intercalation of lithium into the graphite electrode, part of electrolyte would be reduced to form a surface film on graphite electrode, well known as the solid electrolyte interface (SEI) film. The SEI film is the key to the reversible intercalation/deintercalation of Li^+ into/from graphite that occurs at a potential far beyond the stability limits of nonaqueous electrolytes.[2] Initially, the SEI film protects the electrode against further electrolyte decomposition at large negative voltage and the exfoliation of the graphite. But the formation of the SEI film results in an irreversible loss of capacity on the initial charge-discharge cycle of the lithium-ion batteries, and gradual capacity fading may occur as the SEI layer thickens over time.[3] A compact and stable film is believed to improve the stability and rate performances of the carbon electrodes. [4] Generally, the properties of the SEI film depend strongly on the electrolyte composition.The use of additives to the electrolytes is one of the most efficient methods to alter the properties of the SEI films on the surface of the anodes.[5-7]

Based on their functions and reaction mechanisms, electrolyte additives can be divided reduction-type additives and reaction-type additives.[8] For reduction-type additives, the reduction potential is higher than that of the electrolyte, that is, the electrochemical reduction reaction of the additives occurs before the electrolyte decomposes. This results in a protective solid film on the surface of the electrode and thus is able to suppress the decomposition of electrolyte. These additives play important roles in both reducing gas generation and increasing the stability of the SEI film through the participation of additive molecular moieties into the SEI film. vinylene carbonate (VC)[9], fluoroethylene carbonate(FEC)[10] andvinyl ethylenecarbonate(VEC)[11] are typical reduction-type additives widely used in commercial lithium ion batteries. For reaction-type additives, in the potential range of lithium ion intercalation, they may not be reduced electrochemically, however they can help to form more desired SEI film through either scavenging radical anions, forming intermediate compounds with the solvent reduction, or reacting with subsidiary products of the electrolyte decomposition such as lithium alkyl dicarbonate and lithium alkyloxide. For example, dialkylpyrocarbonate, an in situ CO_2-provider[12,13] through the degradation reaction, is a typical reaction-type additive. Other typical reaction-type additives include carboxyl phenol, aromatic esters[14], and anhydride[15] with well-conjugated structures to stabilize intermediate radical anions by delocalization of the radical, maleic anhydride,[16] succinimideand N-benzyloxycarbonyloxy succinimide[17] where "N" atom is linked by two carbonyl groups with strong radical anion-delocalizing ability. Compared with reduction-type additives, the study of the reaction-type additives is still in their infancy.

[a] Lithium-ion Batteries Laboratory, School of Materials Science and Engineering, China University of Mining and technology, Xuzhou 221116, China.Yueli Shi,Tel: +8613852081106, E-mail: zwysyl@163.com.
[b] Department of Chemistry, University of Missouri – Kansas City (UMKC) Kansas City, MO 64110, USA.Xiaobo Chen, Tel: +18162356420, E-mail: Email: chenxiaobo@umkc.edu.
† These authors contributed equally to this work (co-first authors).
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Here, we reportedthe use of TBHQ as a reaction-type additive to electrolyte for lithium-ion batteries. Tertiary butylhydroquinone(TBHQ), an aromaticorganic compound,is a derivative ofhydroquinone, substituted withtert-butylgroup. It has been commonly used as a synthetic food antioxidant to prevent oils and fats from oxidative deterioration and rancidity.[18]It is a highly effectiveantioxidant by reacting with radicals, namely, a radical-scavenging compound.[19] Moreover, it is cheap, non-toxic, lipophilic and dissolves easily in common electrolytes.[20-22] In this study, the typical electrolyte 1.0 M $LiPF_6$-EC:DMC:DEC (1:1:1, v/v/v) wasused to study the effect of TBHQ on the electrochemical properties of the graphite electrode. Charge-discharge, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were used to analyze the electrochemical processes.The results showed that the introduction of TBHQ could effectively improve the capacity and cyclic stability of the graphite electrode by forming a thin , uniform, compactand smooth SEI film.

Results & Discussion

Figure 1 showed the first-cycle CV curves recorded on the graphite electrodes in the electrolyte with and without the TBHQ additive. In the electrolyte without the TBHQ additive, there were three reductive current peaks: peak I at 0.8 V, peak II at 0.5 V, and peak III near 0 V, corresponding to the reduction of EC into Li_2CO_3 (a single electron reduction process), the reduction of EC into alkyl lithium carbonate (a double electrons reduction process), and the intercalation of lithium ions into the graphite electrode, respectively.[23,24] In the electrolyte with TBHQ, peaks I and II related to EC reduction process remain almost unchanged, along with the unchanged peak III. As no other current peaks were observed, TBHQ was electrochemically stable in the entire potential range of lithium ion intercalation.

The first-cycle charge/discharge curves of the graphite electrodes in electrolytes without and with TBHQ were displayed in Figure 2A. The charge capacities of the graphite electrodes in electrolytes without and with TBHQ were 442 $mAh{\cdot}g^{-1}$ and 415 $mAh{\cdot}g^{-1}$, respectively.Apparently, TBHQ

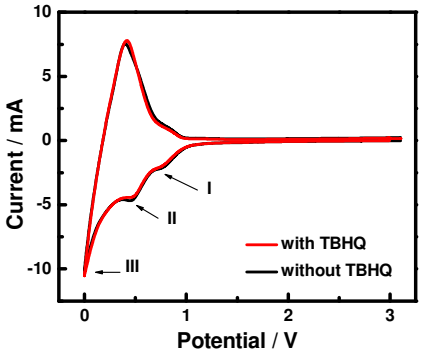


Figure 1. Initial CV curves of graphite electrodes in 1.0 M$LiPF_6$-EC: DMC: DMC electrolyte with and without TBHQ.

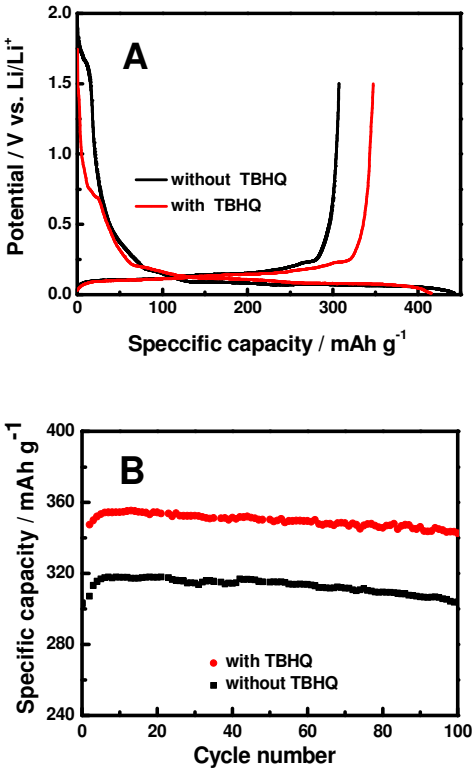


Figure 2. (A)Charge-discharge characteristics of graphite electrode in the electrolytes without and with TBHQ.(B) Cyclic dischargeperformances of graphite electrodes in 1.0 M $LiPF_6$-EC: DMC: DEC (1:1:1, v/v/v) electrolyte without and withTBHQ.

increased the charge capacity of the graphite electrode. However, the discharge capacities of the graphite electrodes in electrolytes without and with TBHQ were 307.2 $mAh{\cdot}g^{-1}$ and 347.5 $mAh{\cdot}g^{-1}$, respectively.Thus, TBHQ enhanced the discharge capacity of the graphite electrode. The irreversible capacities were 135 $mAh{\cdot}g^{-1}$ and 68 $mAh{\cdot}g^{-1}$, for the electrolytes without and with TBHQ, respectively.Introducing TBHQ in the electrolyte obviously reduced the irreversible capacityand improved the faradic efficiency of the graphite electrode.

The cyclic discharge performance was shown in Figure 2B. In the electrolyte without the TBHQ additive, the discharge capacity of the graphite electrode increased gradually from 307.2 to 317.8 $mAh{\cdot}g^{-1}$ at the 10^{th} cycle, and then decreased to 303.4 $mAh{\cdot}g^{-1}$ after 100 cycles. The capacity retention was 98.8% relative to the first cycle. When the graphite electrode cycled in the electrolyte with TBHQ, the discharge capacity increased from 347.5 $mAh{\cdot}g^{-1}$to 355.3 $mAh{\cdot}g^{-1}$ at the 12th cycle, and then decreased to 342.6 $mAh{\cdot}g^{-1}$ after 100 cycles. The capacity retention was 98.6% compared to the first cycle. Therefore, adding TBHQ in the electrolyte obviously increased the cyclic discharge performance (342.6 $mAh{\cdot}g^{-1}$ vs. 303.4 $mAh{\cdot}g^{-1}$) with a12.9% capacity enhancement after 100 cycles.

Figure 3 showed the Nyquist plots of the graphite electrodes at various potentials from 1.2 to 0.2 V in the first discharge process. For both electrolytes with and without TBHQ, atthe potential large than 0.9 V (Figure 3A), there were a small semicircle in the high-frequency region (high-frequency semicircle, abbreviated as HFS) and a large arc in the low-frequency region. When the potential drops to 0.9 V (Figure 3B-3D), the Nyquist plots consisted of three parts, namely HFS, middle-frequency semicircle (MFS) and an inclined line in the low frequency (low frequency line, LFL). According to the study by D. Aurbach, HFS, MFS and LFL are attributed to the lithium diffusion across the SEI film covering on the graphite electrode, charge transfer process,andthesolid-state diffusion of the lithium-ion in the graphite matrix, respectively.[25-27]

The HFS was observed at a rather high potential (3.0 V, and Figure S1). A previous studyby Change and Sohn indicated that graphite promoted decomposition of electrolyte and formation of SEI film without an applied potential.[28] In the study by Little, it was proposed that the HFS was likely caused by contact resistance between the graphite electrode and the current collector.[29]Hence, the HFS might be associated not only with the Li^+ migration through the SEI film, but also with contact resistance between the graphite electrode and the current collector.

In order to reveal the underlying mechanism, an equivalent circuit shown in Figure 4A was used to explain the Nyquist plots in Figure 3. In this equivalent circuit, R_s represents the ohmic resistance, while R_{SEI} and R_{ct} are resistances of the SEI film and the charge transfer reaction,respectively. Thecapacitances of the SEI film and the doublelayerare represented using the constant phase elements (CPE) Q_{SEI} andQ_{dl} respectively. Considering the fact that the low frequencyregioncannot be modelled properly using the finite Warburg element, weuse a CPE instead, i.e. $Q_D$which is related to lithium ion solid-state diffusion

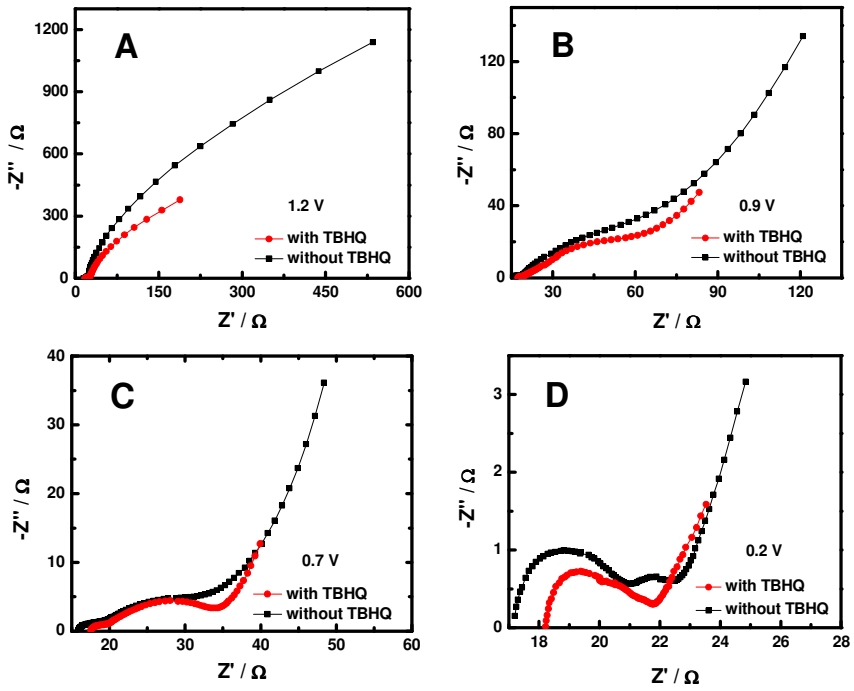


Figure 3. Nyquist plots of the graphite electrodes in the first discharge process in the 1.0 M$LiPF_6$-EC: DMC: DEC (1:1:1, v/v/v) electrolyte without and with TBHQat various potentials: (A) 1.2 V, (B) 0.9 V, (C) 0.7 V, and (D) 0.2 V.

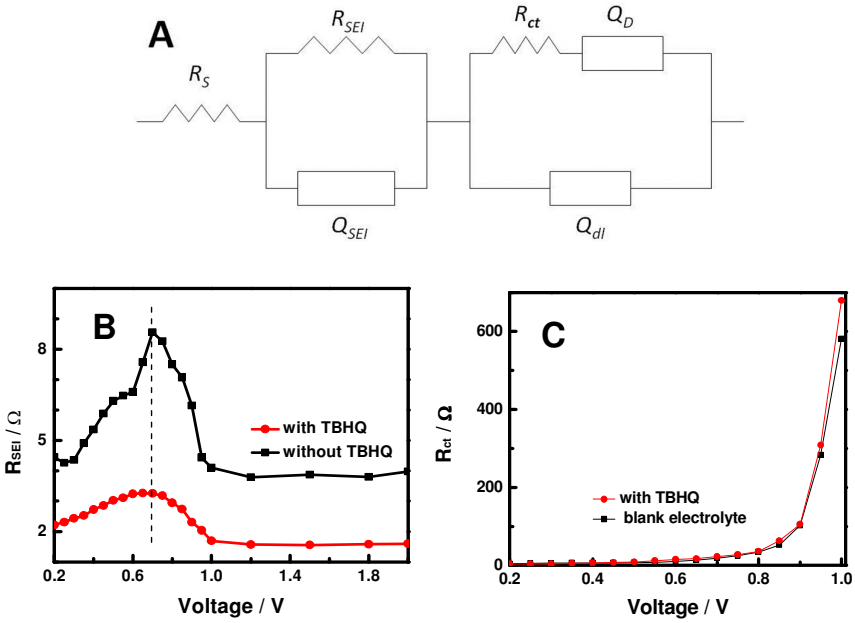


Figure 4. (A) Equivalent circuit proposed for fitting impedance spectra of the graphite electrodes,*R*s is the ohmic resistance, R_{SEI} and R_{ct} are resistances of the SEI film and the charge transfer reaction. Q_{SEI} andQ_{dl}representthecapacitances of the SEI film and the doublelayer.Variations of R_{SEI}(B) and R_{ct}(C) with the electrode potential in electrolytes without and with TBHQ.

inthe graphite electrode. This method has been successfully used tocharacterize the graphite electrodes.TheCPE describes the non-ideal behavior of thecompositeelectrode (porosity of the material, roughness of the surface), and is fit for simulating the graphite electrode.[30-36]The equivalent electrical circuit simulated impedance spectrum were compared with experimental EIS data at 0.7 V and 0.2V in the discharge process in Figure S3 and the parameter values were listed in Table S1 and Table S2. The relative standard deviation formost fitted parameters did not exceed 15%. Therefore, the proposed equivalent circuit can satisfactorily describe theexperimental data.

The changes of R_{SEI}were shown in Figure 4B. For the electrolyte without TBHQ, R_{SEI} remained almost unchanged in the potential range 3.0–1.2 V. From 1.0 V to 0.7 V, R_{SEI} increased rapidly owing to the formation of the SEI film. When the electrode potential decreased from 0.7V to 0.2 V, R_{SEI} decreased rapidly, likely due to that the reduction products of EC, for example, alkyl lithium carbonate reacted with the trace amount of water to form a composition with higher lithium ion conductivity.[37,38]The change trend of R_{SEI} in electrolytes with TBHQ was similar to that of R_{SEI} in electrolyte without TBHQ.R_{SEI} in electrolytes with TBHQ remained almost unchanged in the potential range 3.0 −1.2 V. From 1.0 V to 0.65 V, R_{SEI} increased rapidly.From 0.65 V to 0.2 V, R_{SEI} decreased rapidly.

However, the value of $R_{SEI}$with TBHQ electrolytes was smaller than that of R_{SEI} without TBHQ electrolytes. $R_{SEI} = \rho/lS$, where l is the thickness of the SEI film, S the electrode surface area, ρ the resistivity. The resistivity ρof SEI film formed in electrolytes with andwithout TBHQ are a little different.In the experiments,the surface areas of the graphite electrodes are same.So, it is clear that the changeof the resistance R_1 reflects the change of the thickness of the SEI film. Therefore, smaller value of R_{SEI} with TBHQ electrolytes indicates that adding TBHQ in the pristine electrolyte might favor a thinner SEI film on graphite electrode.Figure 4C showedthevariations of $R_{ct}$with the electrode polarization potential in the electrolyte without and with TBHQ. The existence of TBHQ had negligible effect on the charge-transfer resistance R_{ct}.

The expression for the admittance response of the CPE (Q) is

$$Y = Y_0\omega^n \cos(\frac{n\pi}{2}) + jY_0\omega^n \sin(\frac{n\pi}{2})$$

where ω is the angular frequency, j the imaginary unit. A CPE represents a resistor when n = 0, a capacitor with capacitance of C when n = 1, an inductor when n = −1, and a Warburg resistance when n = 0.5. In this study, Y_0 is considered to be a pseudo capacitance (pseudo-Y_0) when n lies between 0.5 and 1.[39,40]The value of ngives the degree of distortion of the impedance spectraand when n=1, Y is identical to C_i and the CPE becomean ideal capacitor.Larger values of n between 0.5 and 1indicate the properties ofthe pseudo capacitanceare more close to anideal capacitance.The surface of the pseudo capacitance are more uniform.[41,42]

For the electrolyte without TBHQ, Q_{SEI}–nincreased slowly from 1.0 V to 0.65 V(from 0.67 to 0.81)(Fig.S4.), reached the maximum at0.65 V,then remained almost unchanged from 0.65 V to 0.2 V(from 0.81 to 0.76)after the potential of the SEI film formed(consistent with Fig.4B).The value of n in the electrolyte without TBHQ changed between 0.67 and 0.76, indicating $Q_{SEI}$was a pseudo capacitance.Q_{SEI}–n in the electrolyte with TBHQ increased quickly from 0.9 V to 0.65 V(from 0.3 to 0.81)and increased slowly from0.65 V to 0.2 V(from 0.81 to 0.93)after the SEI film formation(consistent with Fig.4B). Q_{SEI}–nin the electrolyte with TBHQ was larger than that in the electrolyte without TBHQafter the SEI film formation below 0.65V,indicating that the properties of Q_{SEI} were closer to anidealcapacitance and uniformity of the SEI film was improved.

Q_{SEI}–Y(Fig.S5.)for the electrolyte without and withTBHQ decreased quickly from 1.0V to 0.65 Vand changed a littlefrom 0.65 V to 0.2 V.Q_{SEI}–Y in in the electrolyte with TBHQ was smaller than that in the electrolyte without TBHQ after the SEI film formation below 0.65V.The above results showed that TBHQintroduction in the electrolyteled to form a more homogenous SEI film with lower capacitance value.

The change ofQ_{dl}–n and Q_{dl}–Y in electrolytes without and with TBHQ were showed in Fig.S6.andFig.S7.Q_{dl}–n in electrolytes without and with TBHQ decreased with the the electrode potential decreasing. Q_{dl}–n in electrolytes with TBHQ was from 0.66 to 0.57 at 0.75V - 0.2V, which was higher than that in electrolytes without TBHQ(from 0.60 to 0.48).While Q_{dl}–Y in electrolytes with TBHQwas lower than that in electrolytes without TBHQ from 0.75V to 0.2V. Q_{dl}–Y varied very little among the range of 0.01F to 0.06F.

Q_D–nand Q_D–Yin electrolytes without and with TBHQ were showed in Fig.S8 and Fig.S9.Q_D–n decreased with the electrode potential decreasingfrom 0.8V to 0.2V.Q_D –n in electrolytes with TBHQ was lower than that in electrolytes without TBHQfrom 0.8V to 0.2V.Q_D –Y in electrolyteswith TBHQ was higher than that in electrolytes withoutTBHQ.

The morphologies of the graphite electrodes after CV test in the electrolyteswith and without TBHQ were showed in Figure 5.The surface of the graphite electrode in the electrolyte without TBHQ had some obvious defects and large grain sizes (Figures 5A and 5B).The surface of the graphite electrode after CV measurement in the electrolyte with TBHQ was smoother and more compact (Figures 5C and 5D).This indicated that the addition of TBHQ helped the formation of a better SEI film.

According to the studies of Endo et al.[43,44],the initial reaction in the electrochemical reduction of the electrolyte involves electron transfer from the catholically polarized electrode to the solvent molecules, and the process coordinates with the lithium cation to produce a radical anion of the solvent.This achieves electron transfer equilibrium with the neighboring solvent molecules coordinated with the same lithium cation. The subsequent decomposition will be initiated from this equilibrium. Thus, if the initial reaction in the reductive decomposition of electrolyte solutions can be affected, the performance of lithium-ion and lithium secondary batteries may be improved.

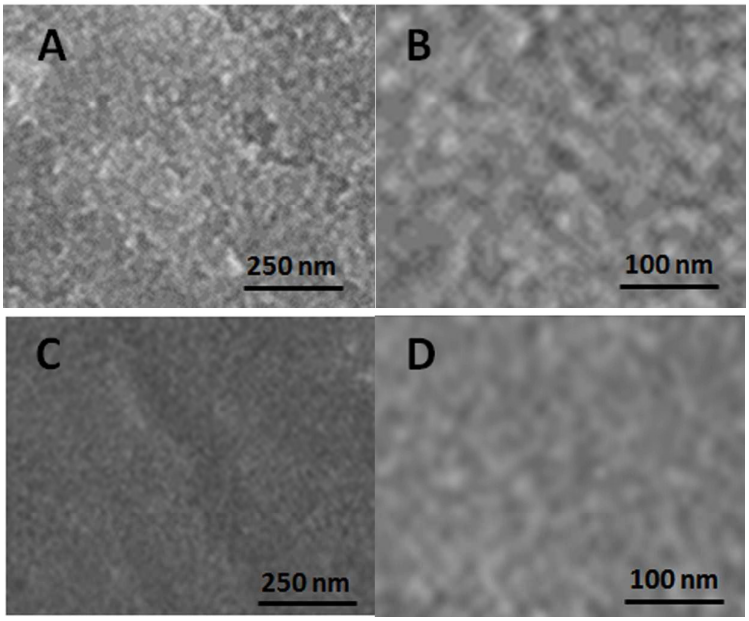
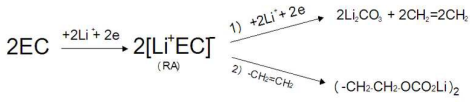


Figure 5.SEM images of the graphite electrodes after CV measurement in the electrolytes without (A, B) and with (C, D) TBHQ.

Two mechanisms have been proposed for the electrochemically induced reduction of EC[45-48], as shown below.



Radical anions areabbreviated as RAs.Both mechanisms are present in the process of SEI film formation and compete with each other. When mechanism (I) (corresponding to peak I in CV) is predominate, the reduction of solvents generates more gaseous products, and the resulting SEI film is Li_2CO_3-abundant and less stable. On the contrary, mechanism (II) (corresponding to peak II in CV) leads to less gaseous products and the resulting products are substantially insoluble in the electrolyte. As a result, the generated SEI film is more compact and smooth. TBHQ is a highly effectiveanti-oxidant and has a well-conjugated structure[49-51]. It is believed to be able to capture less stable radical anions through delocalization of the radical, and to form a polymer with the $[Li^+EC]^-$ through capture radical anions.The polymerization will decompose to form a new product, eventually form athin,uniform, compactand smoothSEI[52-55].

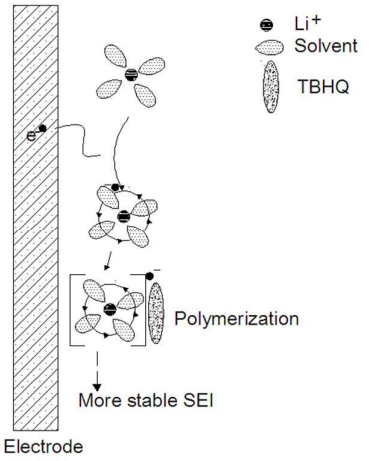


Figure 6. A proposed model for the reaction mechanism of THBQ.

The reaction mechanism of THBQ as a SEI film formation additive for lithium ion batteries was proposed as shown in Figure 6: (i) electron transfer occurring from the catholically polarized electrode to the solvent molecule coordinated with the lithium cation to produce a radical anion; (ii) electron transfer equilibrium with the neighboring solvent molecules coordinated with the same lithium cation; (iii) TBHQ capturing less stable radical anions to form a polymer with the $[Li^+EC]^-$; (iiii) the reductive decomposition of the polymerization to form a more thin , uniform, compact and smooth SEI film and reduced gas generation in the first intercalation of Lithium ions into graphite.The SEI film, such interphases, situating between electrode surfaces and electrolyte, is formed by sacrificial electrolyte decomposition and consuming a certain amount of lithium ion during the initial charging, and constitutes a barrier to allow ionic conduction and forbid electronic conduction.[56]Introducing TBHQ in electrolytes could favor a thin, uniform, compact and smooth SEI film on graphite electrode.A thinner SEI film can reduce the resistance of SEI and reduce the molecular decomposition EC.So formation of a thinner SEI film can consume less electrolyte and lithium ion during the initial charging. Thus the irreversible capacity is reduced and the faradic efficiency is improved during the first-cycle charge/discharge process. The uniform, compact and smooth SEI film has better mechanical properties with increasing the flexibility, which can prevent the SEIrupturecaused by insertion and extraction of lithium ions.The stable SEI film can prevent further reaction between electrode surfaces and electrolyte[57-60].Thusastable SEI layer is beneficial to the cyclic performances.

Conclusions

TBHQ was demonstrated as a new and stable additive for lithium ion batteries. The electrochemical performance of graphite electrode such as cyclic stability and reversible capacity was improved in the electrolyte with TBHQ, due to the formation of a thin,uniform,compact and smoothSEI layer.

Experimental

The graphite electrodes were prepared by spreading a mixture of 90% Micro-carbon fiber (MCF) (Petoca, Japan) and 10% polyvinylidene fluoride (PVDF) (HSV910, USA) binder dissolved in N-methyl-2-pyrrolidone (NMP, Alfa Aaesar) onto a piece of copper foil(thickness: 0.025mm) current collector. The solvent and the water were removed by baking at 80 ℃ in the air and 120 ℃ in vacuum, respectively, and the dried electrodes were suppressed by a roller at room temperature to obtain a smooth and compact structure. The pristine electrolyte was 1.0 M $LiPF_6$ in a mixture of EC, DMC and DEC (1:1:1, volume ratio, Tianci Co., Guangzhou, China). 0.1 wt% TBHQ was added into the pristine electrolyte as the additive.

Charge-discharge test was evaluated through the CR2032-type coin cell. Coin cells were assembled with graphite as the working electrode and lithium as the foil counter electrode, polypropylene microporous separator (Celgard 2400) soaked in the electrolyte as the separator. The coin cells were galvanostatically charged and discharged in a battery analyzer (Neware, Shenzhen, China) over a range of 1.5-0.001 V vs. Li/Li^+ at a constant current density of 0.1C (1C=372 mA g^{-1}).

CV and EIS were carried out in a three-electrode glass cell with Li foils as the counter and reference electrode on an electrochemical workstation (CHI660C, Chenhua Co., Shanghai, China) at room temperature. The area of the work electrode was 1.5×1.5 cm^2. CV was measured in the potential range from 3 V to 0 V at a scan rate of 1 $mV{\cdot}s^{-1}$. EIS was measured in the frequency range from 10^5 to 10^{-2} Hz with the potentiostatic signal amplitude of 5 mV and the frequency range from 10^5 to 10^{-2} Hz. The electrode was equilibrated for 1 h before the EIS measurements to attain steady-state conditions. The impedance results obtained were fitted using Zview software. The specimen after CV test was transferred into the glove box and washed in DMC and dried in vacuum to remove the residual electrolyte. The morphology of the graphite electrode after electrochemical tests in different electrolyte compositions was investigated by a LEO 1530 Field Emission Scanning Electron Microscopy (FE-SEM, Oxford Instrument).

Acknowledgements

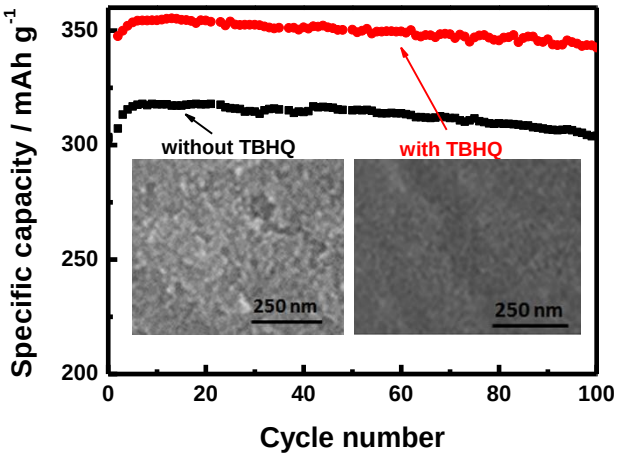
Y.Shi appreciates the support from China Scholarship Council and China University of Mining and technology. X. C. thanks the support from the College of Arts and Science, University of Missouri – Kansas City.

Notes and references

1 B. Moradi and G. G. Botte, *J Appl. Electrochem*, 2016, **46**, 123.
2 Y. He , M. Liu , Z.D. Huang , B. Zhang , Y. Yu , B.h. Li ,F.y. Kang and J. K. Kim, *J. Power Sources*, 2013,**239** , 269.
3 Y.X. Lin , Z. Liu , K. Leung , L.Q. Chen , P. Lu and Yue Qi,*J. Power Sources*, 2016,**309**, 221.
4 S.Y. Li, X.L. Xu, X.M. Shi, B.C. Li, Y.Y. Zhao, H.M.Zhang,Y.L.Li,W.Zhao, X.L.Cui andL.P. Mao,*J. Power Sources*, 2012,**217**, 503.
5 G.Gourdin, J.Collins, D.Zheng, M.Foster andD. Qu,*Electrochem. Soc.* 2015,**1**,118.
6 J. C. Burns, A. Kassam, N. N. Sinha, L. E. Downie, L. Solnickova, B. M. Wayand J. R. Dahn, *J. Electrochem. Soc.*,2013, **160**, A1451.
7 S.Y. Jurng,H.S. Kim,J.G. Lee, J.H.Ryu and S. M. Oh, *J. Electrochem. Soc.*, 2016,**163**,2,A223.
8 D. Aurbach, J.S. Gnanaraj,W. Geissler and M. Schmidt, *J. Electrochem. Soc*, 2004, **151**, A23.
9 L. Liao, X. Cheng, Y. Ma, P. Zuo, W. Fang, G. Yin and Y. Gao, *Electrochim. Acta*, 2013, **87**,466.
10 H. Shin, J. Park, A. M. Sastryand W. Lu, *J. Electrochem. Soc.* 2015,**162**, A1683.
11 S.D. Xu, Q.C. Zhuang, J. Wang, Y.Q. Xuand Y.B. Zhu, *Int. J. Electrochem. Sci*, 2013,**8**, 8058.
12 M.D. Levi, E. Markevich, C. Wang, M. Koltypin and D. Aurbach, *J. Electrochem. Soc*, 2004, **151**, A848.
13 J.T. Lee, M.S.Wu, F.M.Wang, Y.W. Lin, M.Y. Bai and P.C. Chiang, *J. Electrochem. Soc*, 2005, **152**, A1837.
14 C. Wang, H. Nakamura, H. Komatsu, M. Yoshio and H. Yoshitake, *J. Power Sources*, 1998, **74**, 142.
15 J. Ufheil, M.C. Baertsch, A. Wursig and P. Novak, *Electrochim. Acta*, 2005, **50**, 1733.
16 J.H. Ku, S.S. Hwang, D.J. Ham, M.S. Song, J.K. Shon,S.M. Ji, J.M. Choi and S.G. Doo,*J. Power Sources*, 2015,**287**, 36.
17 N. Shahabadi, M. Maghsudi, Z. Kianiand M. Pourfoulad, *Food Chem.*, 2011, **124**, 1063.
18 S. Kashanian and J. Dolatabadi, *Food Chem*, 2009, **116**, 743.
19 C.Rockwell, V.Gangur, J.Pestka, R.Para,A.Turley, J. Zagorski, J. Bursleyand H.Dover,*J. Immun.* 2014,**192**,119.30.
20 Christinawaty, S.Damayanti,*Asian J Pharm Clin Res*, 2015,**8**, 4, 209.
21 S. S. Zhang, K. Xu and T. R. Jow, *J. Power Sources*, 2004, **130**, 281.
22 S. Rana, P. Senand S.K. Bandyopadhyay,*Mater. Chem. Phys.* 2016,**169**, 173.
23 A. M. Haregewoin, E. G. Leggesse, J.C. Jiang,F.M. Wang, B.J. Hwang and S. D. Lin ,*Electrochimica Acta*, 2014,**136**, 274.
24 D. Aurbach, M. D. Levi, E. Levi, H. Telier, B. Markovsky, G. Salitra, U. Heiderand L. Hekier, *J. Electrochem. Soc*, 1998, **145**, 3024.
25 D. Aurbach, *J. Power Sources*, 2000, **89**, 206.
26 M. D. Levi and D. Aurbach, *J. Phys. Chem. B*, 1997, **101**, 4630.
27 M. Holzapfel, A. Martinent, F. Alloin, B. Le Gorrec, R. Yazami and C. Montella,*J. Electroanal Chem*, 2003, **546**, 41.
28 Y. C. Chang and H. J. Sohn, *J. Electrochem. Soc*, 2000, **147**, 50.
29 C. Wang, I. Kakwan, A. J. Appleby and F. E. Little, *J. Electroanal.Chem*, 2000, **489**, 55.
30 Q.C. Zhuang, J. Li and L.L. Tian, *J. Power Sources,*2013,**222**,177.
31 M. L. Shi, *AC Impedance Spectroscopy Principles and Applications*, 2001, National Defense Industry Press, Beijing, 27.
32 Y. B. He , M. Liu , Z.D. Huang , B. Zhang , Y. Yu , B.H. Li ,F. Kang and J.K. Kim, *J. Power Sources.,* 2013,**239**, 269.
33 L.J. Yang, X.Q. Cheng,Y.L Ma, S.F. Lou, Y.Z Cui, T. Guanand G.P. Yin, *J. Electrochem. Soc..*, 2013,**160**,11, A2093.
34 A. M. Haregewoin, E. G. Leggesse, J.C. Jiang,F.M. Wang, B.J. Hwang and S. D. Lin, *Electrochim. Acta.*, 2014,**136**, 274.
35 F. Yao, D. T. Pham and Y. H. Lee,*ChemSusChem.* 2015, **8**, 2284.
36 S. Carrara, V.Bavastrello, D. Ricci, E. Stura and C. Nicolini,*Sensors Actuators B*, 2005,**109**, 221.
37 A. M. Haregewoin, E. G. Leggesse, J.C. Jiang,F.M. Wang, B.J. Hwang and S. D. Lin,*Electrochim.Acta*, 2014,**136**, 274.
38 R. Bernhard, M. Metzgerand H. A. Gasteiger,*J. Electrochem. Soc.*2015,**162**, A1984.

39 Q.C. Zhuang,T.Wei,L.L.Du, Y.L.Cui,L. Fangand S.G.Sun,*J. Phys. Chem. C* ,2010, **114**, 8614.
40 Q.C. Zhuang, J. Li and L.L. Tian,*J. Power Sources*, 2013,**222**,177.
41 K.M. Shaju, G.V. Subba Rao and B.V.R. Chowdari,*Electrochim. Acta*, 2003,**48**, 2691.
42 Q.C. Zhuang,Z.F.Chen,Q.F.Dong,Y.X.Jiang,L.Huang and S.G.Sun,*Chin. Sci. Bulletin*,2006,**51**,17.
43 *Endo,K. Tanak*aand K .Sekai, *J. Electrochem. Soc*, 2000, **147**, 4029.
44 Y. Ein-Eli, S.F. McDevitt, D. Aurbach, B. Markovsky and A. Schecheter, *J.Electrochem. Soc*, 1997, **144**, L180.
45 D. Aurbach and Y. Ein-Eli, *J. Electrochem.*, 1995, **142**, 1746.
46 D. Aurbach,M. D. Levi, E. Levi and Alexander Schechter, *J. Phys. Chem. B.*, 1997, **101**, 2195-2206.
47 Y. Wang, S. Nakamura, M. Ue and P. B. Balbuena, *J. Am. Chem. Soc.,* 2001, **123**, 11708-11718.
48 T.Li,L.Xing,W.Li,Y.Wang,M.Xu,F. Gu, S.Hu, *Journal of Power Sources*., 2013,**244**,668-674.
49 J.Li,Y.Bi,W.Liu,S.Sun,C.Liu and S.Ma, *J Am Oil Chem Soc.*, 2014, **91**,1763–1771.
50 A.Thomas,A.Vikraman,D.Thomas and Krishnapillai Girish Kumar, *Food Anal. Methods*., 2015,**8**,2028–2034.
51 A.Turley,J.Zagorski and C.Rockwell, *Cytokine* , 2015, **71**,289–295.
52 I. A. Shkrob,Y.Zhu, T.W. Marin and D. Abraham, *J. Phys. Chem. C* .,2013, **117**, 19270−19279.
53 K.Ushirogata, K.Sodeyama,Y.Okuno and Y.Tateyama, *J. Am. Chem. So.*,2013, **135**, 11967−11974.
54 E.G.Leggesse and J.C.Jiang, *RSC Adv.*, 2012, **2**, 5439–5446.
55 Y.Wang,S.Nakamura,K.Tasaki and P.B. Balbuena, *J. AM. CHEM. SOC.*,2002, **124**, 4408-4421.
56 L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X.l.Fan, C. Luo, C.s. Wang and K. Xu,Science.,2015,350(6263),938-943.
57 K.Eom,J.Jung,J.Lee,V.Lair,T.Josh, S.Lee, Z.Lin and T.Fuller, *Nano Energy*.,2015,**12**, 314–321.
58 B.Young, D.Heskett, C. Nguyen, M. Nie, J.Woicik and B.Lucht, *Appl. Mater. Interfaces*., 2015, **7**, 20004−20011.
59 R. Schmitz , P.Murmann , R.Schmitz and I. Laskovic, *Progress in Solid State Chemistry*, 2014, **42**, 65-84.
60 J.Zheng,H.Zheng,R.Wang,L.Ben,W.Lu,L.Chen,L.Chen and H.Li, *Phys. Chem. Chem. Phys*., 2014, **16**, 13229—13238.

TOC



Tertiary butyl hydroquinone (TBHQ), as a new electrolyte additive, largely improved the electrochemical performance of the graphite electrode (cyclic stability and reversible capacity), benefited from the formation of a stable and compact thin solid-electrolyte-interface (SEI) film.