SOLID ELECTROLYTE INTER-PHASE ON GRAPHITE ANODES IN Li-ION BATTERIES

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Abstract. Fundamental understanding of processes that occur at the electrode/electrolyte interface during the charging and discharging is prerequisite for developing advanced Li-ion battery systems with good performance. The irreversible capacity loss, cycle life and high rate charge/discharge property of Li-ion battery will be influenced by interfacial reactions including Li-ion insertion/extraction, electrolyte decomposition as well as the formation of a solid electrolyte inter-phase (SEI) layer on the surface of electrode. Recent studies on SEI film of graphite negative electrodes in Li-ion batteries were discussed in this paper. The formation process, composition, thickness, and the function of SEI on graphite anode material were generally analyzed in detail. Furthermore, this article here emphasized the current knowledge of formation mechanism of SEI, because it could help us creating Li-ion batteries with better performance.

1. INTRODUCTION

New energy technologies are critical for the realization of an energy future that is compatible with the goal of sustainable development. Li-ion batteries (LIBs) are becoming a key-enabling technology for electric vehicles and hybrid electric vehicles [1]. At present, graphite is exclusively utilized as the negative electrode material for commercial LIBs due to its extremely low redox potential close to Li+/Li, good cycling stability, low cost, and environmental friendliness [2].

It has reached an agreement that a solid electrolyte inter-phase (SEI) layer will be formed on the surface of graphite anode during the first charge cycle. This interface is conductive for Li-ions but not for electrons, which protecting the graphite from co-intercalation of electrolyte solvent molecules, at the same time consuming Li-ions in the formation of SEI leading to an irreversible capacity loss [1]. With the rapid development of rechargeable LIB, identification and characterization of the SEI film formed on graphite anodes becomes more and more important, since many of the performances of LIB, such as the initial coulombic efficiency, irreversible capacity loss, shelf life and cycle life, are related to the formation and evolution of the SEI film. So far, the structure, chemical composition, morphology and formation mechanism of the SEI film as well as its correlation with the electrochemical performance of LIB have been extensively studied [3-14].

Several different formation models of SEI on graphite electrode (GE) have been proposed [4]. It is accepted that the SEI layer consists of both inorganic and organic species and that there is a dense layer close to the particle surface with a thickness of about 2 nm and on top of this a porous organic layer ranging up to about 80 nm in thickness [5]. The chemical composition at a detailed level is dependent on the type of electrolyte and the surface chemical characteristics of graphite [6].

In this paper, we briefly review SEI film on graphite electrode from the historical aspect and discuss the characteristics of SEI, why SEI forms and what affects its formation, what kind of SEI is

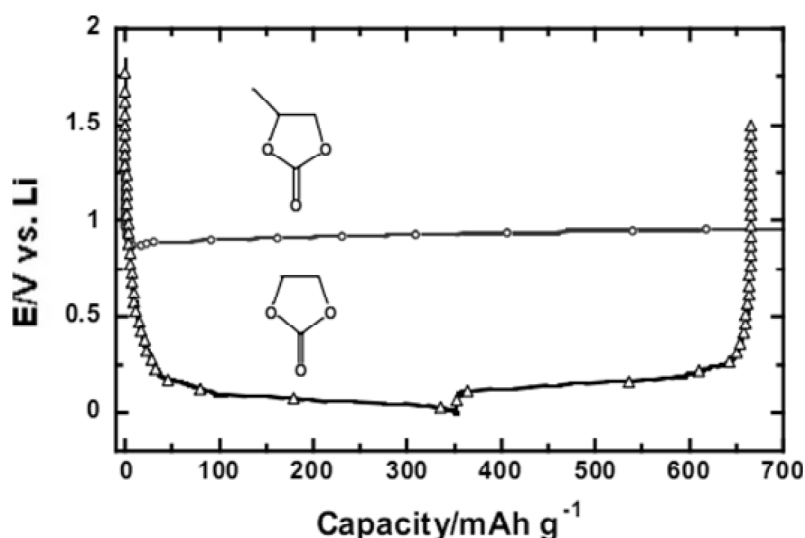Corresponding author: L. H. Huang, e-mail: huang.lihong@foxmail.com

Fig. 1. Voltage profiles of graphitic anodes in LiPF$_6$/EC and LiPF$_6$/PC during polarization to 0.002 V vs. Li indicating distinct interphasial behavior of EC and PC: the reversible Li$^+$ intercalation chemistry at <0.30 V in the former, and the incessant reductive decomposition at ~0.8 V in the latter. Reprinted with permission from J. Electrochem. Soc., 56(9) A751-A755 (2009). Copyright 2009, The Electrochemical Society.

benefit to the performance of LIB, and how to generate a stable SEI on GE. We also highlight the formation mechanism of SEI on GE.
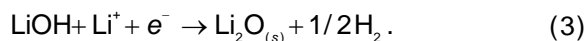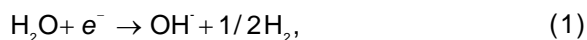
2. FORMATION OF SEI ON THE GRAPHITE ELECTRODE

Originally, PC-based electrolyte was used in LIBs, where the graphite electrode underwent a rapid deterioration of lithium intercalation property. It was generally caused by significant co-intercalation of PC molecules into the interior of graphite before their reductive decompositions with Li-ion [15,16]. Afterwards, Dahn and co-workers published a seminal report that revealed the key role of a protective film allowing reversible Li-ion insertion/de-insertion and preventing co-intercalation of PC in GE, as shown in Fig. 1. The report also emphasized the special effect of ethylene carbonate (EC) on forming such a protective film [17]. This film lies between the GE and the non-aqueous electrolyte solution (NES), consisting of a lithium salt dissolved in either a polar aprotic organic solvent or a mixture of such organic solvents, and it is conductive to Li$^+$ but nonconductive to electrons. Therefore, Dahn [7] also called it a "solid electrolyte inter-phase (SEI)". It is now well established that the SEI greatly determines the safety, power capability, shelf life, and cycle life of commercial LIBs using graphite as the negative electrode materials. Thus, comprehensive understanding of SEI-related phenomena is crucial for the enhancement of electrochemical performances of commercial LIBs [5].

The formation of SEI on GE is a complicated process that can be roughly classified into two distinct steps. First, some chemical substances already present in NES will experience a reductive decomposition when cathodically polarizing the GE to a sufficiently low potential, thus producing various new chemical substances (i.e., the final decomposition products, CH$_2$=CH$_2$, Li$_2$CO$_3$, and ROCO$_2$Li (R=hydrocarbon)). Second, a portion of these new chemical substances will precipitate on the surface of GE from NES under certain conditions, thus building up a protective film that will eventually cover the whole surface of GE. Moreover, it was demonstrated that a SEI called the "internal SEI film" can also be formed around cracks inside the natural graphite spheres [17]. Besides, SEI is relatively stable once formed and its thickness does not increase obviously during cycling. It is now well established that the SEI greatly determines the safety, power capability and cycle life of commercial LIBs using GE, thus a comprehensive understanding of SEI related phenomena is crucial for the enhancement of electrochemical performance of these commercial LIBs [18].
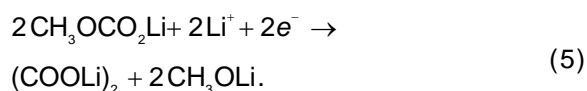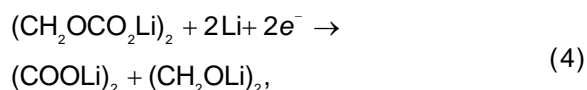
3. COMPOSITION OF SEI ON GE

The SEI has a two-layer structure consisting of a thin and dense layer that is rich in inorganic species (Li$_2$CO$_3$, Li$_2$O, LiOH, LiX (X=F, Cl), etc.) and adhere to the GE side, as well as a thicker and porous layer that is rich in organic species (ROCO$_2$Li, ROLi, (ROCO$_2$Li)$_2$, etc.) and is cohesive to the NES side

[13]. Among these species, Li_2CO_3 has attracted enormous interest as the most important products of SEI due to its efficient prevention of graphite from the subsequent reactions with electrolyte solution [19]. However, there are also numbers of reports where Li_2CO_3 do not present or is not the main compound dominating the SEI at room temperature in some situations [20-22]. The possibilities that can explain absence of Li_2CO_3 in SEI may conclude as following: (1) Li_2CO_3 was not formed in the cell at any stage; (2) Li_2CO_3 formed but reacted with trace amounts of HF in the electrolyte generating LiF, H_2O, and CO_2; (3) Li_2CO_3 formed but reacted with PF_5 to form CO_2, P-O type compounds and LiF. So to some extent, the presence of Li_2CO_3 appears to be depended on the moisture content of electrolyte and the type of cell used. Li_2O has been reported to be another main component which closed to graphite surface. Li_2O formed because there is trace amounts of water in the electrolyte or the electrode, the interrelated chemical changes can be expressed by following equations:

$$H_2O + e^- \rightarrow OH^- + 1/2 H_2, \qquad (1)$$

$$OH^- + Li^+ \rightarrow LiOH_{(s)}, \qquad (2)$$

$$LiOH + Li^+ + e^- \rightarrow Li_2O_{(s)} + 1/2 H_2. \qquad (3)$$

Nevertheless, others [23] reported that Li_2O could be an artifact in the Ar^+ sputtering process rather than a true SEI component. And LiF is formed during cycling or can be generated by Ar^+ etching. A component of SEI, lithium oxalate reduced from lithium alkyl carbonate during the intercalation of Li-ions was also detected by TG-DTA and XPS [24], and these reduction reactions could be accelerated by elevated temperature. Based on results in literatures, the following mechanism can be proposed for the formation of lithium oxalate in SEI [25]:

$$(CH_2OCO_2Li)_2 + 2Li + 2e^- \rightarrow$$
$$(COOLi)_2 + (CH_2OLi)_2, \qquad (4)$$

$$2CH_3OCO_2Li + 2Li^+ + 2e^- \rightarrow$$
$$(COOLi)_2 + 2CH_3OLi. \qquad (5)$$

The above data indicated that careful preparation of the electrode and elaborative sample transference into the spectrometer are all very important for the acquirement of reliable result. The rinsing of GE with solvents can also introduce artifacts and then alter the composition of SEI. Therefore, a standard operational procedure is significant to the reliability of experimental results.

The thickness of the SEI film on GE was measured by increasing the pressure of AFM [26]. The SEI film is about 15 nm thick after the first cycle between 3 and 0.01 V versus Li/Li^+, but it does not yet completely cover the HOPG (highly oriented pyrolytic graphite) surface. After two cycles, the SEI film completely covers the surface of HOPG electrode with an average roughness of 4 nm and a thickness about 25 nm. The impedance of battery increased with the increasing thickness of SEI. This exactly means that the SEI is not always formed in the first cycle completely, but is completed and reinforced in the following few cycles. As was mentioned above, the chemical composition and thickness of SEI were not homogeneous.

4. FORMATION MECHANISM OF SEI ON GE

As we know, the decomposition of non-aqueous electrolyte caused the formation of SEI. Then why would the non-aqueous electrolyte decompose during discharge-charge cycling. Fig. 2 is a schematic of the relative electron energies of the electrodes and non-aqueous electrolyte in a thermodynamically stable battery. Two electrodes, anode (the reductant) and cathode (the oxidant) are electronic conductors with electrochemical potentials μA and μC (their Fermi energies εF) respectively. The energy separation Eg of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the electrolyte is the "window" of the electrolyte. From the schematic diagram we see that an anode with μA above the LUMO and a cathode with μC below the HOMO will reduce/oxidize the electrolyte unless a passivating film formed and created a barrier to electron transfer between the anode/cathode and electrolyte [27]. At the moment, carbonicesters usually used as the electrolyte solvents for lithium salts in LIBs have an oxidation potential (HOMO) at about 4.7 V and a reduction potential (LUMO) near 1.0 V. (All voltages in this paper are referred to Li^+/Li). While, the insertion of Li^+ into graphite happens at about 0~0.25 V, so it is sure that there is a formation of SEI on GE during charge/discharge cycling.

Then what and how determines the characteristics of SEI? Many years of studies devoted to understand the formation mechanism of SEI on GE, and controversy mainly centered with two rival for-
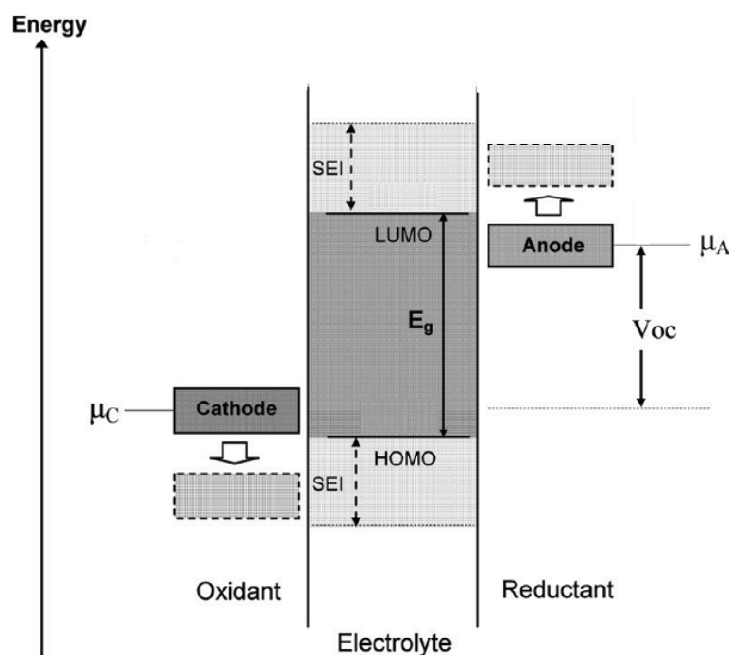
Fig. 2. Schematic open-circuit energy diagram of a non-aqueous electrolyte. *Eg* is the window of the electrolyte for thermodynamic stability. A μA>LUMO and/or a μC <HOMO requires a kinetic stability by the formation of an SEI layer [27]. Reprinted with permission from Ref. [27]. Copyright (2010) American Chemical Society.

mation models. Authors such as Dahn [28] and Aurbach [29] argued that the organic solvents are limited to be reduced on the GE surface to form an intermediate radical anion, and then decomposition of the radical anion is expected to produce the constituents of the SEI. Furthermore, Wang et al. employed a high-level density functional theory calculation to study the reductive decomposition mechanism of EC, they drew a similar conclusion that the initial process in the reduction decomposition of EC is the formation of relevant radical anions [30]. However, others [15,16] did not agree with the preceding surface reaction model, inversely they proposed that the organic solvents coordinating with Li$^+$ in the solvation shells can co-intercalate together with Li$^+$ into graphite layers, which were merely held together by the weak van der Waals forces leaving an intermediate ternary GIC (Li$_{(sol)x}$C$_y$) there. The subsequent decomposition of the ternary GIC is expected to produce the constituents of SEI.

Both the previous models seem to be supported by certain experimental observations, but neither can account for all the existing evidences. Most probably, there exists a competition between the solvent co-intercalation that results in the ternary GIC and the surface reaction that results in the radical anion during the formation of SEI on GE. Then this will render an elegant explanation for the correlation of the gas volume generating during the formation of the SEI on GE observed by Shu et al. [31].

Abundant studies aiming at understanding on the formation of SEI on GE mainly from the perspective of the first formation step (decomposition), to the contrary, only a few have focused on the second formation step. It seems that the first step is more responsible for determining the chemical composition of SEI on GE [13], whereas according to recent studies [32,33], the second step plays a more important role on determining the structure characteristics of SEI on GE [34]. In general, precipitation begins with the appearance of stable solid nuclei among the final reductive decomposition products (the nucleation process), followed by a growth of the formed solid nuclei (the growth process), as shown in Fig. 3. The nucleation rate of the reduction products was found to be dependent on their local molar concentration in NES, to a large degree. The growth rate seems to be under diffusion control rather than interface control.

5. INFLUENCE FACTORS OF SEI

The cycle life of battery is usually related to the SEI film, whether the precipitation is highly compact or the surface species are insoluble and adhere well to the active surface. Hence, the choice of appropriate electrolyte solutions in terms of salts, solvents and additives is very critical for the efficient use of graphite anodes in LIBs.
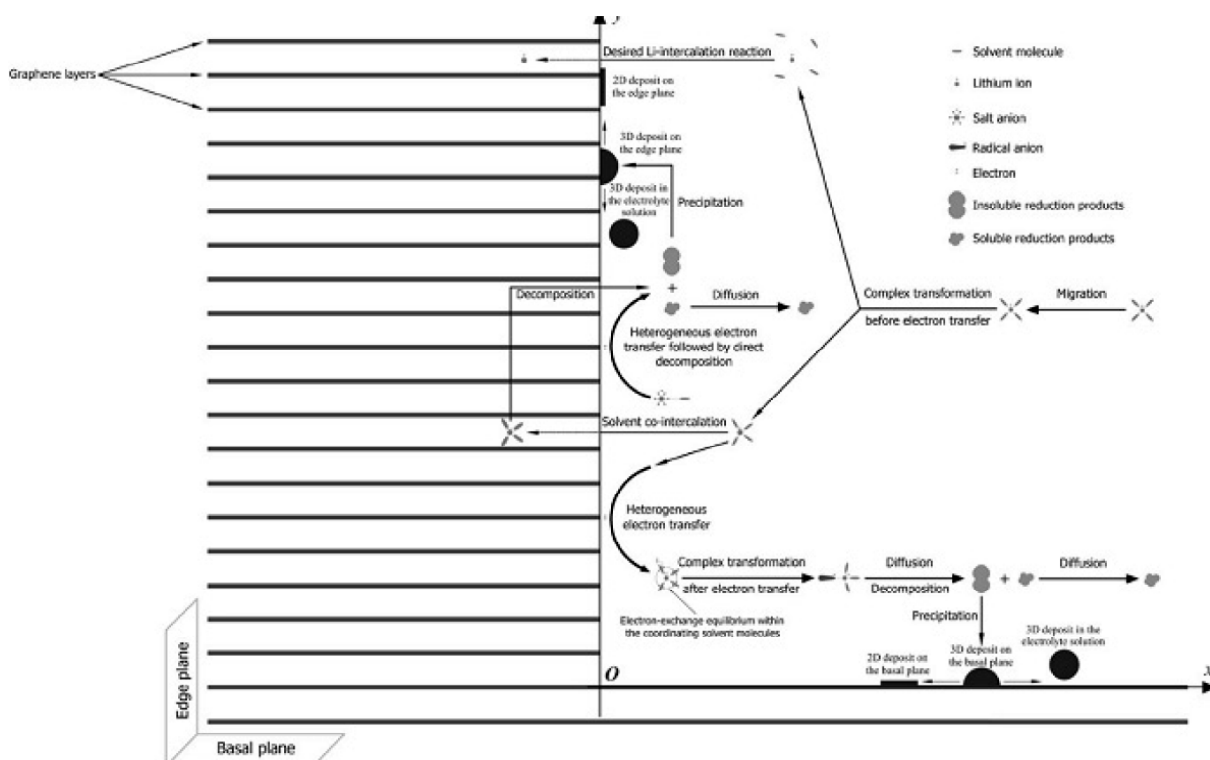
Fig. 3. Reactions near a small portion of a typical graphite electrode in contact with a non-aqueous electrolyte solution during the first cathodic polarization [34]. Reprinted with permission from Ref. [34]. Copyright (2010) Elsevier.

It is well established that the type of Li-ion salt used in the electrolyte will influence the ratio between inorganic and organic components of the SEI layer. Most salts (for instance, $LiBF_4$, $LiPF_6$, $LiAsF_6$, etc.) give rise to a layer of LiF close to the electrode surface. A new salt LiBOB has attracted more attention owing to no LiF forms during cycling [35]. L.F. Li [36] reported that a good SEI lm was obtained by adding LiBOB, which promotes the formation of Li_2CO_3.

The SEI studies were initiated from the investigation of the co-intercalation of PC solvent into the graphite layers. The irreversible reduction and co-intercalation of PC is accompanied with continuous exfoliation of graphite [37]. A remarkable stabilization of GE is obtained by the corporation of EC as a co-solvent [38], the irreversible reduction of solvent was stopped successfully after the first cycle, which was attributed to promoting formation of a stable SEI layer on graphite surface before Li^+ intercalation [28]. One of the mysteries of the SEI formation attracts many attentions: why the stable SEI film can be formed in electrolytes where EC is used, although the only difference between EC and PC is the methyl group in the last molecule. Hence, the obvious question is what is unique in EC that leads to the highly reversible lithium storage behavior of

graphite in its solution. The answer lies in the surface chemistry of the graphite electrodes in the presence of EC. Comparing EC and PC, the methyl group of EC may have another important effect. D. Aurbach [3] studied the reactions of EC and PC with Li/Hg amalgam founding that EC is much more reactive than PC in reduction processes. The formation of effective passivating film may also be connected to the fast kinetics of the reduction of solvent molecules, so as to form insoluble Li salts. The formation process of SEI in EC is faster than detrimental process such as the co-insertion of solution species into the graphite. In a recent publication, Xu reviewed the two major models about the disparity of EC vs. PC on SEI formation [37]: the model of less "cohesive" reduction products of PC by Aurbach [39], and the model of two-electron pathway for PC but single electron pathway for EC by Zhuang et al. [25]. Comparing the electronic factor (electron donating methyl group on PC) with the steric factor (extra methyl group in PC), Aurbach et al. concluded that the steric factor is the dominating one [40]. The electronic factor was also supported by X.J. Wang et al. [41] using MFPC and TFPC with different electron withdrawing functionality. It was found that the interesting trend of SEI formation capability of different solvent was: TFPC > EC > MFPC >>

PC, which could be ascribed to the effects of electron withdrawing group of CF_3 or CH_2F_2 on promoting ring opening.

Organic carbonates with cyclic structures, such as EC, PC, and acyclic structures, like dim-ethyl carbonate (DMC), diethyl carbonate (DEC), ethyl-methyl carbonate (EMC), serve as the main ingredients as electrolyte solvents in state-of-the-art Li ion batteries, mainly because they can form stable inter-phase. Occasionally unsaturated carbonates such as vinyl carbonate (VC) and vinyl-ethyl carbonate (VEC) were also used at small concentration as additives to manipulate the chemistry of inter-phase formation. A mixing ratio of the two kinds of carbonate is determined to balance the ionic conductivity and viscosity of the electrolytes [42,43].

Besides the electrolyte system, the surface properties (such as surface area, particle shape, size and distribution, etc.) of the graphite and the electrode structure (type of binder, binder content, porosity, mechanical properties, etc.) play an important role on the formation of a stable SEI layer [44,45]. The structure of layered graphite gives rise to basically two kinds of surfaces, prismatic (edge) surfaces and basal plane surfaces. Ideal (defect and contaminant free) basal plane surfaces are homogeneous and "smooth" and consist only of carbon atoms. In contrast, the prismatic surfaces are heterogeneous and "rough" and apart from carbon mainly contain various, mostly oxygen-containing surface groups. It is well known that the prismatic and basal plane surface areas of graphite show a different physical, chemical and electrochemical behavior in many respects [46]. Fig. 2 shows the reactions near a small portion of a typical graphite electrode in contact with a non-aqueous electrolyte solution during the first cathodic polarization [34]. GE materials with high crystallinity, low defect concentration, low amount of prismatic surfaces and less surface impurity represent low surface reactivity towards the electrolyte can obtain large reversible capacity and long electrode cycle life. What is more, performance of the SEI is also influenced by atmosphere temperature, impurity content, and distribution of acetylene black conductor and so on [47].

6. SUMMARY

Stabilization of negative electrodes is achieved when reactive electrolyte solution components are reduced at a electrochemical potential above LUMO of electrolyte, forming species which can adhere to anode surface. So it forms a highly compact passivating surface film, which can prevent subsequent reduction of solution species and co-intercalation of solvent into the graphite negative electrode. The SEI film was mainly composed of $(CH_2OCO_2Li)_2$ (EC reduction product), CH_3OLi and CH_3OCO_2Li (reduction products of CH_3OCO_2R, where R arealkyl), Li_2CO_3 (reduction product of CO_2), Li_2S, Li_2O, and Li_xSO_y compounds (reduction products of SO_2). The uniformity of SEI in terms of chemical composition and microstructure is also an important factor influencing the passivation properties. On the one hand, the stability of SEI is up to the formation of effective chemical bond and interfacial action between the SEI film molecule and the negative electrode. On the other hand, it is due to the thermodynamic stability of SEI film molecule.

Moreover, the transmitting properties of Li^+ in SEI are relevant to the characteristic of SEI compositions and the structure of SEI layer. Nonetheless, SEI formation on anodes in LIBs inevitably involves the irreversible consumption of both charge capacity and materials (lithium and electrolyte). Therefore, we must (1) design either an anode with a μA matched to the LUMO of the electrolyte as well as a cathode with a μC matched to the HOMO of the electrolyte (like $Li_4Ti_5O_{12}/LiFePO_4$) or (2) constructing a stable passivating SEI layer that self-heals rapidly when broken by the changes in electrode volume that occur in a charge/discharge cycle; the SEI layer must also permit a fast Li-ion transfer between the electrode and the electrolyte without blocking electron transfer between the active particle and the current collector. (3) looking for a thermodynamics stable electrolyte system that has wide safety window with a larger electrochemical oxidization potential (>5 V) and a smaller electrochemical reducing potential (<0 V). In brief, it is essential to fully and deeply study this complex, continually changing SEI layer, to meet specific application demanding, i.e., high energy density, favourable Li-ion diffusion thermodynamics and kinetics, as well as prolonged cycling stability.

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trical Insulation and Power Equipment (No. EIPE12206).

REFERENCES

[1] E. Peled // *J. Electrochem. Soc.* **126** (1979) 2047.

[2] E. Peled, D. Golodnitsky and G. Ardel // *J. Electrochem. Soc.* **144** (1997) L208.

[3] D. Aurbach, B. Markovsky, I. Weissman, E. Levi and Y. Ein-Eli // *Electrochim. Acta* **45** (1999) 67.

[4] A.M. Andersson and K. Edstrom // *J. Electrochem. Soc.* **148** (2001) A1100.

[5] A.M. Andersson, A. Henningsson, H. Siegbahn, U. Jansson and K. Edstrom // *J. Power Sources* **119-121** (2003) 522.

[6] M.E. Spahr, H. Buqa, A. Wuersig, D. Goers, L. Hardwick, P. Novak, F. Krumeich, J. Dentzer and C. Vix-Guterl // *J. Power Sources* **153** (2006) 300.

[7] E. Peled, D. Bar Tow, A. Merson, A. Gladkichm, L. Burstein and D. Golod-nitsky // *J. Power Sources* **97-98** (2001) 52.

[8] A.M. Andersson, M. Herstedt, A. Bishop and K. Edstrom // *Electrochim. Acta* **47** (2002) 1885.

[9] M. Herstedt, A.M. Andersson, H. Rensmo, H. Siegbahn and K. Edstrom // *Electrochim. Acta* **49** (2004) 4939.

[10] M. Herstedt, D.P. Abraham, J.B. Kerr, K. Edstrom // *Electrochim. Acta* **49** (2004) 5097.

[11] A. Augustsson, M. Herstedt, J.H. Guo, K. Edstrom, G.V. Zhuang, P.N. Ross, J.E. Rubensson and J. Nordgren // *Phys. Chem. Chem. Phys.* **6** (2004) 4185.

[12] M. Herstedt, H. Rensmo, H. Siegbahn, K. Edstrom // *Electrochim. Acta* **49** (2004) 2351.

[13] S. Leroy, F. Blanchard, R. Dedryvere, H. Martinez, B. Carre, D. Lemordant and D. Gonbeau // *Surf. Interf. Anal.* **37** (2005) 773.

[14] K. Edstrom, M. Herstedt and D.P. Abraham // *J. Power Sources* **153** (2006) 380.

[15] J.O. Besenhard, M. Winter, J. Yang and W. Biberacher // *J. Power Sources* **54** (1995) 228.

[16] G.C. Chung, H.J. Kim, S.I. Yu, S.H. Jun, J.W. Choi and M.H. Kim // *J. Electrochem. Soc.* **147** (2000) 4391.

[17] H.L. Zhang, F. Li, C. Liu, J. Tan and H.M. Cheng // *J. Phys. Chem. B* **109** (2005) 22205.

[18] E. Peled and D. Golodnitsky, In: *Li-ion Batteries: Solid Electrolyte Interphase (Chapter 1)*, ed. by P.B. Balbuena and Y. Wang (Imperial College Press: London, 2004).

[19] L.J.J. Rendek, G.S. Chottiner and D.A. Scherson // *J. Electrochem. Soc.* **149** (2002) 408.

[20] G.R. Zhuang and P.N. Ross Jr // *Electrochem. Solid State Lett.* **6** (2003) A136.

[21] M. Herstedt, D. Abraham, J.B. Kerr and K. Edström // *Electrochim. Acta* **49** (2004) 5097.

[22] Y.F. Tang, L. Yang, S.H. Fang and Z. Qiu // *Electrochim. Acta* **54** (2009) 6244.

[23] A.M. Andersona, A. Henningsonb, H. Siegbahnb, U. Janssona and K. Edström // *J. Power Sources* **119-121** (2003) 522.

[24] L.W. Zhao, I. Watanabe, T. Doi, S. Okada and J.I. Yamaki // *J. Power Sources* **161** (2006) 1275.

[25] G.V. Zhuang, H. Yang, B. Blizanac and P.N. Ross // *Electrochem. Solid State Lett.* **8** (2005) A441.

[26] D. Alliata, R. Kotz, P. Novak and H. Siegenthaler // *Electrochem. Commun.* **2** (2000) 436.

[27] J.B. Goodenough and Y. Kim // *Chem. Mater.* **22** (2010) 587.

[28] R. Fong, U. von Sacken and J.R. Dahn // *J. Electrochem. Soc.* **137** (1990) 2009.

[29] O. Chusid, E. Ein-Ely, D. Aurbach, M. Babai and Y. Carmeli // *J. Power Sources* **43** (1993) 47.

[30] Y. Wang, S. Nakamura, M. Ue and P.B. Balbuena // *J. Am. Chem. Soc.* **123** (2001) 11708.

[31] Z.X. Shu, R.S. McMillan and J.J. Murray // *J. Electrochem. Soc.* **140** (1993) 922.

[32] J. Yan, B.J. Xia, Y.C. Su, X.Z. Zhou, J. Zhang and X.G. Zhang // *Electrochim. Acta* **53** (2008) 7069.

[33] J. Yan, Y.-C. Su, B.-J. Xia and J. Zhang // *Electrochim. Acta* **54** (2009) 3538.

[34] J. Yan, J. Zhang, Y.C. Su, X.G. Zhang and B.J. Xia // *Electrochim. Acta* **55** (2010) 1785.

[35] K. Xu, S.S. Zhang and T.R. Jow // *Electrochem. Solid State Lett.* **6** (2003) A117.

[36] L.F. Li, B.Xie, H.S. Lee, H.Li, X.Q. Yang, J. McBreen and X.J. Huang // *J. Power Sources* **189** (2009) 539.

[37] K. Xu // *J. Electrochem. Soc.* **156** (2009) A751.

[38] D. Aurbach, B. Markovsky, A. Schechter, Y. Ein-Eli and H. Cohen // *J. Electrochem. Soc.* **143** (1996) 3809.

[39] D. Aurbach, H. Teller and E. Levi // *J. Electrochem. Soc.* **149** (2002) A2155.

[40] D. Aurbach, Y. Gofer, M. Ben-Zion and P. Aped // *J. Electroanal. Chem.* **339** (1992) 451.

[41] X.J. Wang, H.S. Lee, H. Lia, X.Q. Yang and X.J. Huang // *Electrochem. Commun.* **12** (2010) 386.

[42] K. Xu, Y. Lam, S.S. Zhang, T.R. Jow and T.B. Curtis // *J. Phys. Chem. C* **111** (2007) 7411.

[43] K. Xu // *J. Electrochem. Soc.* **154** (2007) A126.

[44] M.E. Spahr, H. Wilhelm, T. Palladino, N. Dupont-Pavlovsky, D.Goers, F. Joho and P. Novák // *J. Power Sources* **119–121** (2003) 543.

[45] M.E. Spahr, T. Palladino, H. Wilhelm, A. Würsig, D. Goers, H.Buqa, M. Holzapfel and P. Novák // *J. Electrochem. Soc.* **151** (2004) A1383.

[46] J.P. Olivier and M. Winter // *J. Power Sources* **97-98** (2001) 151.

[47] R. Spotnitza and J. Franklin // *J. Power Sources* **113** (2003) 81.