Electrochemical Behaviors of Graphite in an Ethylene Carbonate-Based Electrolyte Containing Two Different Types of Film-Forming Additive

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Abstract— **Electrochemical reactions occurring at a graphite electrode were investigated to gain insight into the effects of film-forming additives such as vinylene carbonate, fluoroethlyene carbonate (FEC) and lithium bis(oxalato) borate (LiBOB) on surface film formation on the electrode. The surface film generated in the presence of a mixture of FEC and LiBOB was found to have the certain characteristics that are important in the initial charging and discharging process. The mixture produced a highly resistive film on the graphite electrode, resulting in an improvement in Coulombic efficiency.**

Keywords— graphite electrode; surface film; additive; vinylene carbonate; fluoroethylene carbonate; litihum bis(oxalato)borate; lithium-ion battery

I. INTRODUCTION

The storage of electric energy is enormously important, and thus electrochemical devices such as batteries play a crucial role in modern energy storage technology. A battery can store energy as a form of chemical energy in its positive and negative electrodes, and converts the chemical energy directly into electrical energy by spontaneous electrochemical oxidation and reduction reactions, which occur respectively at the negative and the positive electrodes. The interconversion of chemical and electrical energy is possible in rechargeable batteries. Since the first invention of rechargeable lead/acid batteries by Planté in 1859, many types of electrochemical rechargeable battery systems have been proposed, and considerable advances have been made over the past two decades.

Lithium-ion batteries (LiBs), which have been commercialized in Japan since 1991, are the most advanced rechargeable battery systems. They can store much higher levels of energy (twofold to sixfold in gravimetric energy density) than conventional rechargeable batteries such as lead/acid, nickel-cadmium (Ni-Cd), and nickel-metal hydride (Ni-MH) batteries. In the past twenty years, they have become the main source of energy for portable electronic devices such as cellular phones, camcorders, and notebook computers, replacing conventional Ni-Cd and Ni-MH batteries. In addition, recent environmental concerns about global warming and the need to reduce CO_2 emissions provide us a strong driving force for developing large-scale lithium-ion batteries of high performance and long cycle life for use in electric vehicles and dispersed energy storage systems.

Graphite is one of the most important negatively charged electrode materials in commercially available LiBs [1]. It has a typical layered substance that consists of hexagonal sheets of sp^2-carbon atoms weakly bonded together by van der Waals forces. Lithium ions are intercalated between its layers during charging, and de-intercalated during discharging. It has been widely recognized that a film is formed on the graphite surface by the decomposition of electrolyte during the initial charge process, which occurs before the intercalation of lithium ions into graphite [2-4]. This surface film, often called the solid electrolyte interface, allows lithium ions to pass through, whereas the transfer of electrons is blocked. Thus, the surface film formation suppresses the additional decomposition of electrolyte that occurs due to the electron transfer between electrode and electrolyte, and allows selective intercalation and de-intercalation of lithium ions.

The formation of surface films strongly depends on the type of electrolyte used. Surface films with excellent properties are formed when an ethylene carbonate (EC)-based electrolyte solution is used. With EC-based electrolytes, the intercalated lithium ions can be extracted with very high efficiency, after their electrochemical intercalation into the graphite. The battery performances such as discharge capacity and Coulombic efficiency are strongly affected by the nature of the surface film.

Many researchers have made efforts in search for the film-forming additives that provide a superior surface film on graphite with minimal consumption of charge [5-8]. Use of film-forming additives is one of the most

economic and effective methods for the improvement of battery performance. Two types of film-forming additives have been suggested: reduction-type and reaction-type additives.

The reduction-type additives usually have higher reductive potentials than the electrolyte solvents. Prior to electrochemical reduction of the electrolyte solvents, the additives are preferably reduced to form an insoluble solid product, which is subsequently covered onto the surface of graphite as a preliminary film to deactivate catalytic activity. This additive type includes vinylene carbonate (VC) [9,10] and fluoroethlyene carbonate (FEC) [11]. They assist film formation through the adsorption of their reduced products onto the catalytic active sites of the graphite surface.

On the other hand, the reaction-type additives may not be reduced electrochemically in the whole potential range of lithium intercalation, yet are able to either scavenge radical anions, which are intermediate compounds of the solvent reduction, or combine with the final film products to form more stable film components. A common characteristic of this additive type is that the potential of the film formation during the initial lithium intercalation is very close to that of the solvent reduction. This is because the additives themselves do not involve reduction. Lithium bis(oxalato) borate (LiBOB) is a typical example of the reaction-type additives [12,13]. It has been reported that the use of LiBOB instead of $LiPF_6$ as an electrolyte solute in propylene carbonate solvent significantly suppresses the decomposition of electrolyte and graphite exfoliation, enabling lithium ions to be intercalated into graphite without the aid of film-forming agents such as VC, FEC, and EC, indicating that LiBOB forms a stable surface film on the graphite surface.

This study examined the electrochemical behaviors of graphite in non-aqueous solutions containing two different types of film-forming additive. Mixtures of reduction-type and reaction-type additives, VC + LiBOB or FEC + LiBOB, were used as a film-forming additive. Cyclic voltammetry (CV), charge/discharge, and electrochemical impedance measurements were carried out to ascertain the interfacial reactions between graphite and an EC-based electrolyte solution in the presence of two different types of additive.

II. EXPERIMENTAL

A base electrolyte solution was prepared of 1 mol dm^{-3} (M) $LiClO_4$ dissolved in dissolved in a 1:1 (by volume) mixture of EC and diethyl carbonate (DEC) (Panax Etec Co., Lithium Battery Grade). Three kinds of additives, VC, FEC, and LiBOB, were added (2 wt% each) to the base solution, which was then dried over 4A molecular sieves for weeks. All the additives were purchased from Enchem Co. and were used as received. The water content in each solution was less than 30 ppm, which was confirmed using a Karl-Fischer moisture titrator (Kyoto Electronics Manufacturing Co., MKC-210).

Natural graphite powder (The Kansai Coke and Chemicals Co., NG-7) was used for the CV, charge/discharge, and electrochemical impedance measurements. The test electrode was prepared by coating a mixture of the graphite powder (90 wt%) and a polymeric binder (10 wt%) on copper foil. A laboratory-made cell was used for the CV as shown in Fig. 1. The working graphite electrode was mounted on the bottom of the cell. It was brought into contact with the electrolyte solution using an O-ring. The geometrical surface area was 0.8 cm^2. Lithium foil was used as counter and reference electrodes. The CV and charge/discharge measurements were carried out between 3.0 and 0.0 V at a sweep rate of 0.5 mV s^{-1} and a constant current of 37.2 mA g^{-1}, respectively.

The electrochemical impedance was obtained after the electrode was polarized at a constant potential for a sufficient amount of time until the current became negligible (typically < 1 μA). The impedance was measured with a potentiostat (PGZ 402, VoltaLab) over the frequency range of 0.1 Hz to 100 kHz. The alternating amplitude was 5 mV.

All the electrochemical measurements were carried out using conventional three-electrode cells in an argon-filled glovebox (Three-Shine, SK-G1200) with a dew point below –60 °C. Lithium foil was used as counter and reference electrodes. All the potentials are referred to as volts vs. Li^+/Li.
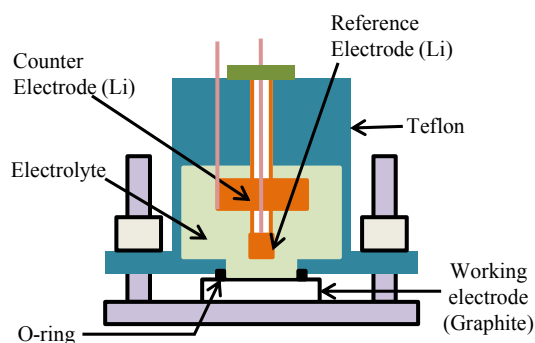

Fig. 1. Schematic illustration of three-electrode cell used for electrochemical impedance measurements.

III. RESULTS AND DISCUSSION

The main objective of the study was to understand the interfacial reactions between graphite and an EC-based electrolyte solution in the presence of a mixture of reduction- and reaction-type additives. Prior to figuring out how the mixture affected the interfacial reactions, the electrochemical behaviors of the graphite electrode were investigated in the presence of a reduction- or reaction-type additive only.

The complete electrochemical behavior of a system can be obtained through a series of steps to different potentials with recording of the current-time curves, as described in Fig. 2. Fig. 2 shows the cyclic voltammograms of the graphite electrode in 1 mol dm^{-3} LiClO$_4$/EC + DEC with or without additives. CV is a very useful technique for obtaining information about fairly complicated electrode reactions. In Fig. 2(a), a reduction peak is observed centered at 0.7 in the first cycle and is absent in the second cycle, indicating that their presence and subsequent disappearance is closely related to film formation on the graphite surface. The film-forming potential was greatly influenced by the additive. In the first cycle, the peak potentials were 1.0, 0.95, and 1.65 V, in VC-, FEC-, and LiBOB-containing solutions, respectively. These disappeared in the second cycle. Besides the four reduction peaks, large reduction peaks at a potential of ~0 V and oxidation peaks at a potential of ~0.25 V could be assigned to the lithium intercalation and de-intercalation events, respectively [14].
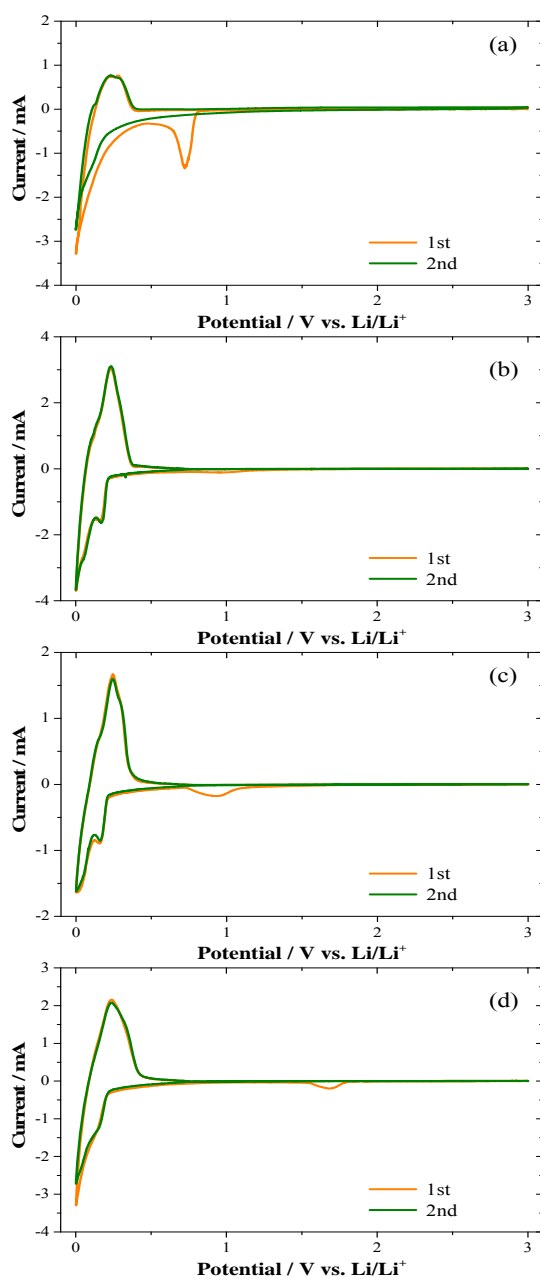

Fig. 2. (a) The first and second cyclic voltammograms of natural graphite powder at 0.5 mV s^{-1} in 1 M LiClO$_4$/EC + DEC (a) without additive and with (b) 2 wt% VC, (c) 2 wt% FEC, and (c) 2wt % LiBOB.

Fig. 3 shows the cyclic voltammograms of the graphite electrode in the presence of a mixture of VC + LiBOB or FEC + LiBOB. CV results similar to Fig. 2(d) were obtained in both solutions, indicating that LiBOB reductively decomposes preferentially on the graphite surface. It is reasonable to consider that the reductions peaks at ~0.65 V are attributed to irreversible decomposition of LiBOB. A reduction peak originating from VC or FEC is not observed in the first cycle of voltammograms. On the other hand, each lithium intercalation and de-intercalation peak varies slightly in shape and size in both Figs. 2 and 3.

It has been reported that film formation on graphite takes places in two major voltage stages [15,16]. The first stage takes place before the intercalation of lithium ions between graphene layers during initial charging. The film formed in this stage is made up of inorganic-rich components and is structurally porous, highly resistive, and dimensionally unstable. The second stage proceeds differently to the first stage. It occurs simultaneously with the intercalation of lithium ions, and the resulting film of organic-rich components is more compact and highly conductive. In view of this two stage mechanism, the first stage may be associated with the decomposition of LiBOB producing large irreversible capacities, while both VC and FEC including solvent molecules decompose in the second stage with small irreversible charge consumptions.
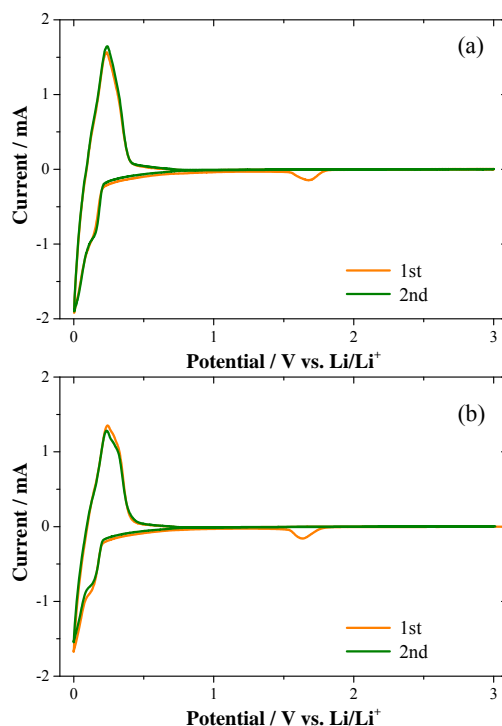

Fig. 3. The first and second cyclic voltammograms of natural graphite powder at 0.5 mV s^{-1} in 1 M LiClO$_4$/EC + DEC (a) 2 wt% VC + 2 wt% LiBOB and (b) 2 wt% FEC + 2 wt% LiBOB.

The results from the CV analyses indicate that the charge and discharge reactions occurring at the graphite were greatly influenced by the additive. Fig. 4 shows potential profiles during first charging (lithium intercalation) and discharging (de-intercalation) of the graphite electrode, with and without additives. In all electrolyte solutions, the potential of the graphite electrodes dropped rapidly at the beginning of charging, and then very slowly between 0 and 0.25 V.

It is an established fact that electrochemical lithium intercalation into graphite accompanies a series of potential plateaus. These correspond to reversible stage transformations between the different staged structures of Li-graphite intercalation compounds (Li-GICs), depending on the lithium concentration, at potentials < 0.25 V. Staging is a thermodynamic phenomenon related to the energy required to open the van der Waals gap between two graphene layers for the guests entering the hosts. The repulsive Coulombic interactions between the guest ions are less effective. As a consequence, few van der Waals gaps are energetically favored over a random distribution of guests. In Fig. 4, many potential plateaus appeared on the charge and discharge curves. These potential profiles show that, in forming Li-GICs, lithium ions were reversibly intercalated into and de-intercalated from the graphite in the two solutions.
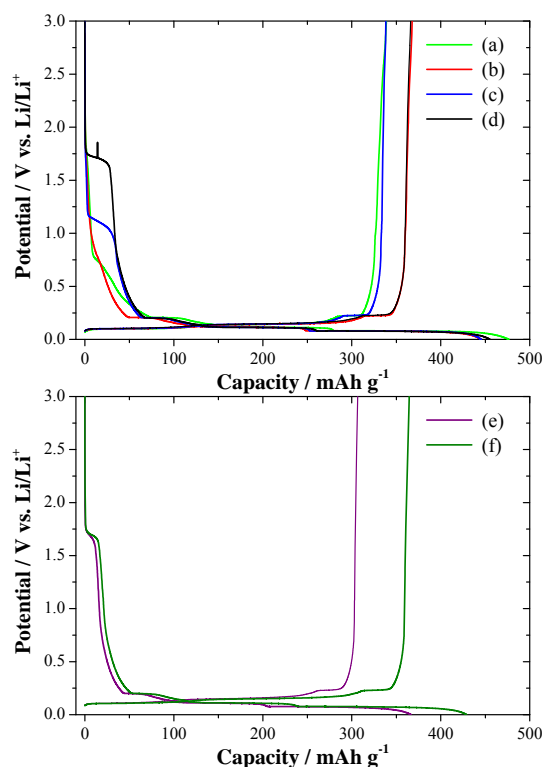
Fig. 4. Charge and discharge curves in the first cycle of natural graphite powder in 1 M LiClO$_4$/EC + DEC (a) without additive and with (b) 2 wt% VC, (c) 2 wt% FEC, (d) 2wt % LiBOB (e) 2 wt% VC + 2 wt% LiBOB, and (f) 2 wt% FEC + 2 wt% LiBOB.

In the absence of additives, the graphite electrode exhibited small discharge capacity and low Coulombic efficiency. It is widely believed that the irreversible capacity is consumed for electrolyte decomposition and film formation on graphite [2,3]. All five additives effectively improved the poor compatibility between the electrode and electrolyte solution.

The charge and discharge capacities, and the Coulombic efficiencies during the first cycles are summarized in Table 1. Discharge capacity was greatly increased in the presence of VC, LiBOB and FEC + LiBOB. On the other hand, Coulombic efficiency was greatly improved in the presence of VC, VC + LiBOB and FEC + LiBOB. The addition of FEC + LiBOB gave the best charge and discharge characteristics with a high Coulombic efficiency.

Table I. Charge And Discharge Capacities, And Coulombic Efficiencies Of Natural Graphite Powder Obtained From Fig. 3.

Curves	Charge capacity (mAh g^{-1})	Discharge capacity (mAh g^{-1})
	Coulombic efficiency (%)	
(a)	477	339
	71.1	
(b)	446	368
	82.5	
(c)	445	338
	76.0	
(d)	456	366
	80.3	
(e)	367	307
	83.7	
(f)	429	365
	85.1	

The aforementioned charge and discharge results illustrated large changes in the properties of the surface film during cycling, dependent on the type of additive used. Impedance spectra of the graphite electrode (Fig. 5) were obtained at 0.7 V in order to determine the electrochemical properties of the surface films formed by each additive. Depressed arcs in the high frequency region were attributed to the impedance of lithium ion migration

through the surface films on graphite [17-20]. The impedance was greatly dependent on the additive. A small impedance was obtained in the absence of additive (Fig. 5(a)) and in the presence of VC and FEC (Fig. 5(b, c). In contrast, in the presence of LiBOB (Fig. 5(d–f)), the impedance was greatly increased, indicating that the LiBOB-derived films can have a negative influence on electrode performance. This may seem contradictory, as a surface film with high resistance is not suitable for electrochemical redox reactions at electrode surfaces. Therefore, it is reasonable to conclude that the improved Coulombic efficiency in the presence of FEC + LiBOB was due to the positive effect of FEC far outweighing any negative effect.
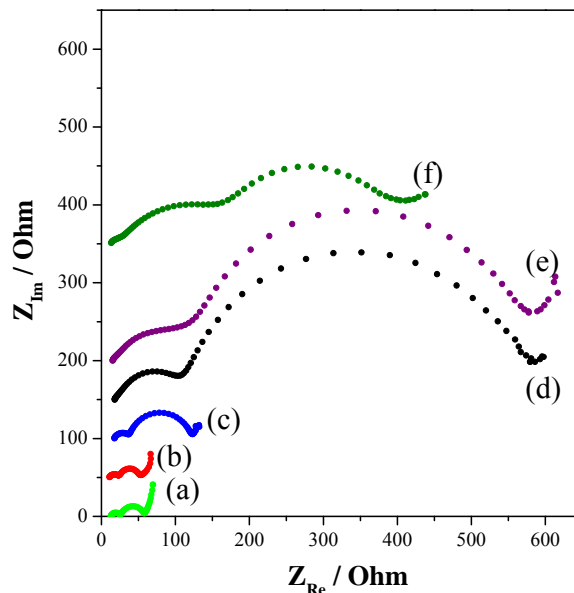

Fig. 5. Impedance spectra at natural graphite powder (NG-7) obtained after 2 cycles in 1 M LiClO$_4$/EC + DEC (a) without additive and with (b) 2 wt% VC, (c) 2 wt% FEC, (d) 2wt % LiBOB (e) 2 wt% VC + 2 wt% LiBOB, and (f) 2 wt% FEC + 2 wt% LiBOB.

IV. CONCLUSIONS

Electrochemical lithium redox reactions at a graphite electrode in 1 M LiClO$_4$/EC + DEC were found to be strongly dependent on the additive. The discharge capacity and Coulombic efficiency were superior in the presence of FEC + LiBOB, indicating the mixture of reduction- and reaction-type additives to be an appropriate candidate for a film-forming additive for the graphite electrode in lithium secondary batteries. Although the details of the chemical reaction mechanism for film formation are unclear, this study indicates that the type of additive in the electrolyte solution is an important factor in determining the performance of a surface film on graphite. The causative reasons for the observed behavior should be investigated. Future studies focusing on understanding the film-forming mechanism are in progress and will be reported in due course.

References

[1] T. Ohzuku, Y. Iwakoshi, and K. Sawai, "Formaion of lithium-graphite intercalation compounds in nonaqueous electrolytes and their application as a negative electrode for lithium ion (shuttlecock) cell," J. Electrochem. Soc., vol. 140, pp. 2490-2498, September 1993.
[2] R. Yazami and D. Guerard, "Some aspects on the preparation, structure and physical and electrochemical properties of LixC$_6$," J. Power Sources, vol. 43, pp. 39-46, January 1993.
[3] E. Peled, "The electrochemical behavior of alkali and alkaline earth metals in nonaqueous battery systems? The solid electrolyte interphase Model," J. Electrochem. Soc., vol. 126, pp. 2047-2051, December 1979.
[4] R. Fong, U. von Sacken, and J.R. Dahn, "Studies of lithium intercalation into carbons using non-aqueous electrochemical cells," J. Electrochem. Soc., vol. 137, pp. 2009-2014, July 1990.
[5] L. Ma, J. Self, M. Nie, S. Glazier, D.Y. Wang, Y.S. Lin, and J.R. Dahn, "A systematic study of some promising electrolyte additives in Li[Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$]O$_2$/graphite, Li[Ni$_{0.5}$Mn$_{0.3}$Co$_{0.2}$]/graphite and Li[Ni$_{0.6}$Mn$_{0.2}$Co$_{0.2}$]/graphite pouch cells," J. Power Sources, vol. 299, pp. 130-138, December 2015.
[6] G. Chen, G.V. Zhuang, T.J. Richardson, G. Liu, and P.N.J. Ross, "Anodic polymerization of vinyl ethylene carbonate in Li-ion battery electrolyte," Electrochem. Solid-State Lett., vol. 8, pp. A344-A347, July 2005.
[7] M. Lu, H. Cheng, and Y. Yang, "A comparison of solid electrolyte interphase (SEI) on the artificial graphite anode of the aged and cycled commercial lithium ion cellsOriginal," Electrochim. Acta, vol. 53, pp. 3539-3546, March 2008.
[8] K.-C. Möller, H.J. Santner, W. Kern, S. Yamaguchi, J.O. Besenhard, and M. Winter, "In situ characterization of the SEI formation on graphite in the presence of a vinylene group containing film-forming electrolyte additives ," J. Power Sources, vol. 119-121, pp. 561-566, June 2003.
[9] D. Aurbach, J.S. Gnanaraj, W. Geissler, and M. Schmidt, "Vinylene carbonate and Li salicylatoborate as additives in LiPF$_3$(CF$_2$CF$_3$)$_3$ solutions for rechargeable Li-ion batteries," J. Electrochem. Soc., vol. 151, pp. A23-A30, January 2004.
[10] G. Chen, G.V. Zhuang, T.J. Richardson, G. Liu, and P.N.J. Ross, "Anodic polymerization of vinyl ethylene carbonate in Li-ion battery electrolyte," Electrochem. Solid-State Lett., vol. 8, pp. A344-A347, July 2005.
[11] R. McMillan, H. Slegr, Z.X. Shu, and W.D. Wang, "Fluoroethylene carbonate electrolyte and its use in lithium ion batteries with graphite anodes," J. Power Sources, vol. 81–82, pp. 20-26, September 1999.

[12] K. Xu, S.S. Zhang, U. Lee, J.L. Allen, and T.R. Jow, "LiBOB: Is it an alternative salt for lithium ion chemistry? ," J. Power Sources, vol. 146, pp. 79-85, January 2005.
[13] K. Xu, S.S. Zhang, and T.R. Jow, "Electrochemical impedance study of graphite/electrolyte interface formed in LiBOB/PC electrolyte," J. Power Sources, vol. 143, pp. 197-202, January 2005.
[14] Z. Jiang, M. Alamgir, and K.M. Abraham, "The electrochemical intercalation of Li into graphite in Li/polymer electrolyte/graphite cells," J. Electrochem. Soc., vol. 142, pp. 391-395, February 2006.
[15] S.S. Zhang, M.S. Ding, K. Xu, J. Allen, and T.R. Jow, "Understanding solid electrolyte interface film formation on graphite electrodes," Electrochem. Solid-State Lett., vol. 4, pp. A206-A208, December 2001.
[16] S.S. Zhang, K. Xu, and T.R. Jow, "EIS study on the formation of solid electrolyte interface in Li-ion battery," Electrochim. Acta, vol. 51, pp. 1636-1640, January 2006.
[17] H. Schranzhofer, J. Bugajski, H.J. Santner, C. Korepp, K.-C. Möller, J.O. Besenhard, M. Winter, and W. Sitte, "Electrochemical impedance spectroscopy study of the SEI formation on graphite and metal electrodes," J. Power Sources, vol. 153, pp. A23-A30, January 2004.
[18] A. Lewandowski and I. Acznik, "Impedance study of protecting film formation on lithium and lithiated graphite induced by bis(fluorosulfonyl) imide anion," Electrochim. Acta, vol. 56, pp. 211-214, December 2005.
[19] H.Y. Wang and F.M. Wang, "Electrochemical investigation of an artificial solid electrolyte interface for improving the cycle-ability of lithium ion batteries using an atomic layer deposition on a graphite electrode," J. Power Sources, vol. 288, pp. 1-5, July 2013.
[20] Y. Hoshi, Y. Narita, K. Honda, T. Ohtaki, I. Shitanda, and M. Itagaki, "Optimization of reference electrode position in a three-electrode cell for impedance measurements in lithium-ion rechargeable battery by finite element method," J. Power Sources, vol. 288, pp. 168-175, August 2015.