Electrolyte interphase (SEI). The formation of SEI is undesirable because Li⁺ ions/electrons are supplied from the graphite electrodes, which appears as an increase in the open-circuit voltage (OCV) of the graphite electrodes. The thermal stability and the passivating ability of SEI layers. This study investigates these issues. More specifically, in this work, SEI films were generated on graphite electrodes with different states-of-charge (SOC) in the graphite electrodes. Thermal degradation/repairing of the SEI films were assessed by performing an open-circuit voltage (OCV) measurement at elevated temperatures. The change in surface films with respect to chemical composition and morphology was examined with X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM).

Experimental

To prepare the graphite composite electrodes, a mixture of mesocarbon microbeads (MCMB-10-28, average particle diameter = 10 μm, graphitization temperature = 2800 °C, Osaka Gas Co.), Super P (a conductive carbon), and poly(vinylidene fluoride) (PVdF, Kureha, KF-1300) binder (85:5:10 in wt. ratio) was dispersed in N-methyl pyrrolidone. The resulting slurry was coated onto a piece of copper foil (a current collector) and dried at 120 °C for 12 h under vacuum. Two-electrode 2032-type coin cells were fabricated with an as-prepared MCMB composite electrode, Li foil (as a counter electrode) and a glass fiber filter (Advantec, GA-55, as a separator). The used electrolyte was 1.0 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 in vol. ratio). The cells were assembled in an argon-filled dry box and cycled in a temperature-controlled oven.

At present, graphite is the most widely-used negative electrode for lithium-ion batteries (LIBs). At the working potential of the graphite electrode (0.2−0.3 V vs. Li/Li⁺), most of the conventional carbonate-based electrolytes are not stable against reductive decomposition, and the decomposed products deposit as a film, also known as the solid electrolyte interphase (SEI). The formation of SEI is undesirable because Li⁺ ions and the equivalent amount of electric charges are consumed in this process, which appears as an irreversible capacity. However, SEI formation is critically important for graphite electrodes to be successfully used as a negative electrode for LIBs. Namely, the SEI layers are electronically insulating. Hence, any electrochemical reactions at the electrode/electrolyte interface are hindered due to negligible electron tunneling through the SEI layer. As a result, additional electrolyte decomposition is prevented once it forms at a certain thickness. That is, the surface film passivates the graphite electrodes. Another beneficial feature of the SEI layer is that it is a Li⁺ ion conductor, such that it does not induce concentration polarization in lithium reactions but enables reversible Li⁺ intercalation/de-intercalation for graphite negative electrodes.

In order for the SEI layer to serve as an effective passivating film, however, it should meet other requirements in addition to its Li⁺ ion conducting and electronically insulating properties. It should uniformly cover the electrode surface to passivate the whole graphite surface. A thinner SEI layer is generally favored to minimize the ohmic resistance as far as it plays the passivating role. Thermal stability is another requirement because SEI films are vulnerable to damage upon high-temperature exposure. The organic or inorganic ingredients in SEI layers may be either thermally decomposed or dissolved.

Once thermally degraded, the SEI layer loses its passivating ability to cause additional electrolyte decomposition. The damaged SEI is repaired by this electrolyte decomposition and concomitant film deposition. This repair process leads to several unfavorable features. For instance, the graphite electrodes are self-discharged because Li⁺ ions/electrons in the graphite electrodes are consumed in this process, which appears as an irreversible capacity. Changes in SEI morphology and chemical compositions upon high-temperature exposure have been reported in the literature. In all these previous reports, however, little attention has been given to thermal stability and the passivating ability of SEI layers. This study investigates these issues. More specifically, in this work, SEI films were generated on graphite electrodes with different states-of-charge (SOC) and exposed to a high-temperature environment. It was found that the SEI films are degraded during the high-temperature exposure, but repaired by the forthcoming electrolyte decomposition and film deposition. Interestingly, the repairing behavior was critically affected by the degree of lithiation (states-of-charge, SOC) in the graphite electrodes. Thermal degradation/repairing of the SEI films were assessed by performing an open-circuit voltage (OCV) measurement at elevated temperatures. The change in surface films with respect to chemical composition and morphology was examined with X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM).
temperature-controlled oven to monitor the OCV change while the oven temperature was fixed at 85 °C.

For post-mortem field-emission SEM (FE-SEM, JSM-6700F, JEOL) and X-ray photoelectron spectroscopy (XPS) analyses, the cells were dismantled in an argon-filled dry box, and the cycled electrodes were collected and washed with DEC. A hermetic vessel was used to transfer the electrode samples from the dry box to the instrument chamber. The XPS data were collected in an ultra-high vacuum multipurpose surface analysis system (Sigma probe, Thermo, UK) that operates at a base pressure of < 10⁻¹⁰ mbar. The photoelectrons were excited by Al Kα (1486.6 eV) radiation at a constant power of 150 W (15 kV and 10 mA); the X-ray spot size was 400 μm². During data acquisition, a constant-analyzer-energy mode was used at a pass energy of 30 eV and a step of 0.1 eV. The atomic concentration, which is the ratio of the number of atoms of the element of interest to that of others, was calculated from the XPS spectra with the atomic sensitivity factor.²⁰

Results and Discussion

Fig. 1 shows the evolution of the open-circuit voltage (OCV) during storage at 85 °C, which was traced from three graphite electrodes with different SOCs: SOC0, SOC25, and SOC50. The initial OCV values before storage were 1.5, 0.15, and 0.12 V (vs. Li/Li⁺), respectively. The OCV increased upon storage for the three samples. In the case of SOC0, the OCV increased rapidly to reach 3.0 V, which is the value for fully de-lithiated graphite (x = 0 in LiᵸC₆). When extending the time to reach 3.0 V for SOC25, it eventually reached the fully de-lithiated state (3.0 V). In the case of SOC50, however, the final OCV after 24 h of storage was still 0.6 V, showing that the graphite electrode is still partially lithiated. Two features should be noted here. First, the OCV increase is a signature of a transfer of Li⁺ ions and the equivalent amount of electrons from the graphite electrode to the electrolyte at the interface during the storage. Such a charge transfer is impossible if the SEI layer is perfectly passivating. Hence, the OCV increase signifies a loss of passivating ability even after high-temperature storage. In contrast, the reduction peak at 0.7 V is absent in the graphite electrode. After storage, the reduction peak at 0.7 V appears again in the graphite electrodes belonging to group B, still carry Li⁺ ions and electrons (x > 0 in LiₓC₆). The SEI layers on group B exposed to a high-temperature environment are thermally degraded, yet the graphite electrodes are still partially lithiated. It is thus expected that the Li⁺ ions and electrons in the graphite electrodes can participate in the repair process.

In order to confirm the thermal degradation of the SEI layers and loss of passivating ability during high-temperature storage, the graphite electrodes belonging to group A and B were placed back into the temperature-controlled oven (25 °C) and cycled galvanostatically. Fig. 2a shows the lithium dQ/dV profiles obtained in the pre-cycling period (before high-temperature storage), in which a reduction peak appears at 0.7 V (vs. Li/Li⁺) in the first cycle, but disappears in the second cycle. Obviously, this feature is associated with the reductive decomposition of carbonate-based electrolytes and concomitant SEI deposition on the graphite electrodes. After storage, the reduction peak at 0.7 V appears again in group A (Fig. 2b), illustrating that electrolyte decomposition is severe because the SEI layer has been degraded during storage. In contrast, the reduction peak at 0.7 V is absent in the group B electrodes (Fig. 2c), illustrating that the SEI layers still possess a good passivating ability even after high-temperature storage.

Fig. 3 shows a detailed analysis on the loss of passivating ability for the SEI layers on the group A and B electrodes. Fig. 3a shows the evolution of Coulombic efficiency before and after storage. Be-
Figure 3. (a); The Coulombic efficiency obtained at 25°C before and after the storage, and (b); irreversible capacity and Coulombic efficiency obtained right after the storage. In (a), the graphite electrodes were cycled five times at 25°C (pre-cycling) and stored at 85°C (indicated as the vertical dotted line). After the storage, the graphite electrodes were charge/discharge cycled again at 25°C. Current density = 37.2 mA g⁻¹ (0.1 C).

fore storage (pre-cycling period), the Coulombic efficiency is as low as 85∼87% in the first cycle for five samples, but it increases up to >99% within a few forthcoming cycles. This ensures a full passivation of the graphite electrodes as a result of SEI deposition in the pre-cycling stage. After the high-temperature storage, however, the passivating ability of the SEI layers is sharply different between the two groups. As shown in Fig. 3a, group A shows a Coulombic efficiency of ~85% right after storage, but the value steadily increases in the next few cycles. In contrast, the Coulombic efficiency of group B is >95% from the first cycle. The first irreversible capacity and the Coulombic efficiency obtained after storage are compared in Fig. 3b. A higher irreversible capacity and lower Coulombic efficiency is observed for group A. Generally, the irreversible capacity in graphite electrodes originates from irreversible charge consumption for electrolyte decomposition and SEI formation. It is thus clear that the SEI layer in group A has lost its passivating ability during the high-temperature storage. Hence, electrolyte decomposition and film deposition are severe when they are cycled after storage. In contrast, the SEI layer on group B is rather robust maintaining its passivating ability even when exposed to a high-temperature environment.

Fig. 4 shows the SEM images taken before and after storage, from which the morphological change of the SEI films upon high-temperature exposure is addressed. Fig. 4a shows the SEM image of a pristine electrode surface, in which the MCMB (larger particles) and Super P (smaller particles) are bound by PVdF binders. After pre-cycling, foreign materials are deposited on the electrode surface, which must be the surface film (SEI) derived from the electrolyte decomposition. After storage, the surface film on SOC0-24 h (Fig. 4c), which represents group A (surface film A, hereafter), crumbles and loses its initial morphology. In contrast, the surface film on SOC50-24 h, which represents group B (surface film B, hereafter), still uniformly covers the electrode surface (Fig. 4d). Evidently, surface film A is severely damaged, whereas surface film B appears intact.

To gain an insight into what happens on the surface films during high-temperature storage, the film compositions are analyzed with XPS. Fig. 5 shows the O 1s and F 1s spectra obtained from three different electrodes; before storage, one from group A and one from group B. All the XPS spectra are fitted according to the reported binding energy in Table I. The spectra taken before storage show the presence of O- and F-containing chemical species in the SEI layer, which are derived from electrolyte decomposition. The changes in chemical compositions upon high-temperature storage,
however, differ between the two groups. Namely, a notable spectral change appears on surface film A (Fig. 5b) compared to the spectra taken before storage (Fig. 5a), whereas the change is marginal for surface film B (Fig. 5c). In detail, when the O 1s spectra for surface film A are compared with those taken before storage (Fig. 5a), the peak at 533.5 eV increases at the expense of the peak at 532 eV. In addition, the intensity of the F 1s peak at 686.6 eV greatly increases on surface film A. In contrast, surface film B (Fig. 5c) is quite similar in chemical composition to that observed before storage (Fig. 5a). The strongest O 1s peak at 532 eV and F 1s peak at 685 eV are still observed in surface film B.

From the similarity in chemical composition between the initial film and surface film B, one can assume that the film formation mechanism is similar for the two processes; the initial SEI formation during the pre-cycling period and the repairing period for the damaged SEI layer. Namely, the initial surface film is generated by decomposition of electrolyte ingredient (carbonate-based organic solvent and LiPF₆), for which Li⁺/e⁻ are supplied from the graphite electrode. In the case of the group B electrodes, Li⁺ ions and electrons can be supplied from the graphite electrodes even under an open-circuit condition because they are still partially lithiated. In other words, the SEI layer on the group B electrodes is damaged upon high-temperature storage either by dissolution or decomposition, but the surface film is repaired by a reaction between the electrolyte component and the Li⁺ ions/electrons supplied by the partially lithiated graphite electrodes. If this is the case, the chemical composition of surface film B should be similar to that of the initial SEI layer because the films are derived from the electrolyte ingredients for both cases. Direct evidence for the supply of Li⁺ ions/electrons from the graphite electrode is the steady increase of OCV during storage in Fig. 1.

The absence of a self-remedying action on the group A electrodes can be assumed based on the absence of Li⁺ ions/electrons in the fully de-lithiated graphites. The SEI layer is damaged during storage, but the surface film cannot be regenerated because Li⁺ ions/electrons are exhausted in the graphite electrodes. Even in this case, however, thermally remade products could be deposited if any electrolyte components are thermally unstable. This possibility is confirmed by the XPS data shown in Fig. 5, in which a high population of LixPFyOz (Fig. 5c) is quite similar to the initial SEI layer because the films are derived from LiPF₆ that is thermally unstable.

The results presented so far can be summarized by tracing what happens in the SOC25 sample during high-temperature storage under an open-circuit condition (Fig. 1). This graphite electrode is exposed to a high temperature while being partially lithiated. Upon high-temperature exposure, the SEI film is degraded but repaired with the aid of Li⁺ ions/electrons inside the graphite. The OCV of graphite electrodes increases because of the consumption of Li⁺ ions/electrons in this process. This degradation and repair are continued with an increase in OCV until the Li⁺ ions/electrons are exhausted. The graphite electrodes belonging to group B, in which the SEI is repaired, still possess the passivating ability (Fig. 2c). In contrast, the graphite electrodes in group A cannot be repaired. Instead, the thermally unstable component (for instance, LiPF₆) is decomposed without the aid of Li⁺ ions/electrons from the graphite, and the resulting products (LiₓPF₆Oₓ) are deposited. The passivating ability of the latter electrodes is poor, such that an appreciable amount of electrolyte decomposition is observed when cycled at room temperature after the high-temperature storage (Fig. 2b).

Conclusions

The thermal behavior of surface films that are deposited on graphite electrodes with different SOCs is investigated. Specifically, the degradation/repairing behavior of the surface films is analyzed as a function of the SOC. The major findings are summarized below.

(i) The OCV measurement can effectively be used to examine the thermal degradation of surface films. During storage at 85 °C, the OCV of the MCMB electrodes continuously increases to reach 3.0 V (vs. Li/Li⁺). During this period, the SEI film is degraded and repaired until the Li⁺ ions/electrons in the graphite are exhausted. The time to reach 3.0 V (fully de-lithiated state) is proportional to the degree of lithiation (SOC) for the graphite electrodes.

(ii) When the SEI films on partially lithiated graphite electrodes (group B in this study) are exposed to a high-temperature environment, the damaged layers are repaired by the reaction between the electrolyte and Li⁺ ions/electrons supplied from the graphite. Hence, the passivating ability of the surface films is largely maintained. In addition, these newly formed SEI films have a similar chemical composition to the initially formed SEI films.

(iii) Once the surface films are thermally damaged and the graphite electrodes are fully de-lithiated, the damaged films are not repaired. Instead, thermally decomposed products can be deposited. The passivating ability of these films is poor.

(iv) One practically important message of this work is that the full discharging of LIBs is not desirable because of the graphite negative electrode in such a fully discharged cell. If this cell is occasionally exposed to high-temperature environment, the surface films on the de-lithiated graphite electrode are damaged without repairing. Due to the poor passivating ability of surface films, the cell performances are deteriorated.

Acknowledgments

This work was financially supported by LG Chem. Co. The authors also acknowledge the financial support from National Research Foundation of Korea funded by the MEST (NRF-2010-C1AAA001-2010-0029065), and also from Korea Research Institute of Chemical Technology (KRICT).

References

1. E. Peled, J. Electrochem. Soc., 126, 2047 (1979).
2. J. O. Besenhard, M. Winter, J. Yang, and W. Biberacher, J. Power Sources, 54, 228 (1995).
3. E. Peled, D. Golodnitsky, C. Menachem, and D. Bar-Tow, J. Electrochem. Soc., 145, 5482 (1998).
4. A. S. Claye, J. E. Fischer, C. B. Huffman, A. G. Rinzler, and R. E. Smalley, J. Electrochem. Soc., 147, 2845 (2000).
5. J. Yamaki, in Encyclopedia of Electrochemical Power Sources, G. Jürgen, ed., p. 183, Elsevier, Amsterdam (2009).
6. P. Verma, P. Maire, and P. Novák, Electrochim. Acta, 55, 6332 (2010).
7. A. M. Andersson and K. Edström, J. Electrochem. Soc., 148, A1100 (2001).
8. Y. Reynier, R. Yazami, and B. Fultz, in Battery Conference on Applications and Advances, 2002. The Seventeenth Annual, p. 145 (2002).
9. K. Araki and N. Sato, J. Power Sources, 124, 124 (2003).
10. K. Tasaki, A. Goldberg, J.-J. Lian, M. Walker, A. Timmons, and S. J. Harris, J. Electrochem. Soc., 156, A1019 (2009).
11. R. Yazami and Y. F. Reynier, Electrochim. Acta, 47, 1217 (2002).
12. M. Inaba, H. Tomiyasu, A. Tasaka, S.-K. Jeong, and Z. Oguma, Langmuir, 20, 1348 (2004).
13. W. Li, A. Xiao, B. L. Lucht, M. C. Smart, and B. V. Ratnakumar, J. Electrochem. Soc., 155, A648 (2008).
14. M. Winter, Z. Phys. Chem., 223, 1395 (2009).
15. L. Bodenes, R. Dedryvère, H. Martínez, F. Fischer, C. Tessier, and J.-F. Pierès, J. Electrochem. Soc., 159, A1739 (2012).
16. S.-I. Tobishima and J.-I. Yamaki, J. Power Sources, 81–82, 882 (1999).
17. S.-I. Tobishima, K. Takei, Y. Sakurai, and J.-I. Yamaki, J. Power Sources, 90, 188 (2000).
18. A. M. Andersson, M. Herstedt, A. G. Bishop, and K. Edström, Electrochim. Acta, 47, 1885 (2002).
19. H. Park, T. Yoon, J. Mun, J. H. Ryu, J. J. Kim, and S. M. Oh, J. Electrochem. Soc., 160, A1539 (2013).
20. J. F. Moulder, W. F. Sickle, P. E. Sobol, and K. D. Bomben, Handbook of X Ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data, Physical Electronics, Inc., Eden Prairie, Minnesota (1995).
21. T. Zheng, A. S. Goudz, and G. G. Amatucci, J. Electrochem. Soc., 146, 4014 (1999).
22. R. Feng, U. von Sacken, and J. R. Dahn, J. Electrochem. Soc., 137, 2009 (1990).
23. R. Kamro, Y. Kawamoto, Y. Takei, S. Ohashi, N. Imanishi, and O. Yamamoto, J. Electrochem. Soc., 139, 3397 (1992).
24. D. Aurbach, Y. Ein-Eli, O. Chusid, Y. Carmeli, M. Babai, and H. Yamin, J. Electrochem. Soc., 141, 603 (1994).
25. F. Salvador-Dima, C. Lemain, B. Beaudoin, L. Aymard, and M. J. Tarascon, Solid State Ionics, 98, 145 (1997).
26. R. Dedryvère, L. Gireaud, S. Grugeon, S. Laruelle, J.-M. Tarascon, and D. Gonbeau, *J. Phys. Chem. B*, 109, 15868 (2005).
27. L. El Ouatani, R. Dedryvère, J.-B. Ledeuil, C. Siret, P. Biensan, J. Desbières, and D. Gonbeau, *J. Power Sources*, 189, 72 (2009).
28. S. Park, J. H. Ryu, and S. M. Oh, *J. Korean Electrochem. Soc.*, 15, 19 (2012).
29. S. E. Sloop, J. K. Pugh, S. Wang, J. B. Kerr, and K. Kinoshita, *Electrochem. Solid-State Lett.*, 4, A42 (2001).
30. K. Xu, *Chem. Rev.*, 104, 4303 (2004).