Self-discharge of secondary lithium-ion graphite anodes

Chunsheng Wang\textsuperscript{a,}\textsuperscript{*}, Xiang-wu Zhang\textsuperscript{a}, A. John Appleby\textsuperscript{a}, Xiaole Chen\textsuperscript{b}, Frank E. Little\textsuperscript{c}

\textsuperscript{a}Center for Electrochemical Systems and Hydrogen Research, Texas Engineering Experiment Station, Texas A&M University, College Station, TX 77843-3402, USA
\textsuperscript{b}Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA
\textsuperscript{c}Center for Space Power, Texas Engineering Experiment Station, Texas A&M University, College Station, TX 77843-3118, USA

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Abstract

A new method for measuring self-discharge of lithium-ion graphite anodes is reported. First, the anode lithium content is calculated from the open-circuit potential as a function of open-circuit time (OCP versus OCT) using equilibrium potential–composition isotherms. Then, the self-discharge rate is obtained from the differential of lithium content with respect to time on open circuit. The self-discharge rate measured by this means after the first charge–discharge cycle to 0.0 V versus Li/Li\textsuperscript{+} is largely controlled by the growth of the solid electrolyte interphase (SEI) film, with some influence from stage transformation.

\textsuperscript{*}Corresponding author. Tel.: +1-979-845-0622/2033; fax: +1-979-845-9287.
\textit{E-mail address}: cswang@tamu.edu (C. Wang).

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1. Introduction

Lithium-ion batteries are now widely used for such civilian applications as portable telephones and lap-top computers because they offer significant advantages in specific energy and energy density over the state-of-the-art nickel systems. However, for aerospace applications such as the outer planet and solar probe (OP–SP) missions and geosynchronous earth orbit (GEO) satellites, extended operating or calendar lives of 10–15 years are required. Generally, lithium-ion cells undergo self-discharge. This is less significant than that of nickel–cadmium and nickel–metal hydride cells, but is still both relatively rapid and temperature dependent. Recent work shows that the self-discharge of LiCoO\textsubscript{2} or LiNi\textsubscript{x}, M\textsubscript{4}O\textsubscript{2}-graphite cells is controlled by the progressive growth of the solid electrochemical interphase (SEI) film on the anode, which consumes intercalated lithium [1]. Much of the capacity loss in the graphite anode may be recovered by recharging when a source of excess lithium is available in the counter electrode. However, the entire initial capacity of the graphite is not fully recoverable because the Li\textsuperscript{+}-conducting SEI film formed on individual graphite particle clusters is an electronic insulator, and its continued growth will eventually disintegrate the clusters. Hence, graphite anode self-discharge involves reversible and irreversible losses [2].

Usually, anode self-discharge as a function of open-circuit time is measured by fully charging the anode, relaxing for different open circuit times, then discharging at a low current. However, the accuracy of this conventional method is low. First, Li consumption due to SEI film growth occurs during both the time of relaxation and that of measurement of charge retention. Hence, the total time on open circuit should be much larger than that for charge retention measurement. Accuracy therefore suffers since insufficient data can be obtained. Secondly, the reaction overpotential increases with open-circuit time due to continued SEI film growth. Charge retention depends on the charge and discharge rate used on previous cycling [3]. Obtaining accurate data requires the use of small charge and discharge currents whose values will be a function of the previous history of relaxation. These currents must both fully charge the anode and measure the real charge retained. However, the use of low discharge currents increases the discharge time, so charge retention measured this way will diverge from accurate values.

In the present study, a new more accurate method has been developed to measure the self-discharge rate of Johnson Matthey (JM) 287 graphite anodes at 25 °C, whose self-discharge mechanism is evaluated.
2. Experimental

2.1. Electrode and cell preparation

Electrodes were prepared from a mixture of 92 wt.% ball-milled Johnson Matthey (JM) 287 graphite powder (particle size ca. 15 μm, BET area >30 m²/g) and 8 wt.% polyvinylidene fluoride between two nickel screen current collector using 1-methyl-1-2-pyrrolidinone as solvent. After drying overnight at 120 °C, the electrode was pressed into a sandwich structure with a geometric surface area of 2.0 cm² and weight of 40 mg. Electrochemical measurements were conducted in a three-electrode PTFE cell with two lithium foils as counter and reference electrodes as in earlier work [4]. The electrolyte was 1.0 M lithium hexafluorophosphate (LiPF6) in a 1:1:3 (v/v) ethylene carbonate (EC)–propylene carbonate (PC)–dimethylcarbonate (DMC) mixture (High Purity Lithium Battery Grade, Mitsubishi Chemical Company). All potentials given are versus the Li/Li⁺ reference electrode in this electrolyte. Charge (lithium insertion) and discharge (lithium extraction) characteristics were measured between 0.0 and +1.5 V at constant current using an Arbin Instruments (College Station, TX) automatic battery cycler.

2.2. Li extraction equilibrium potential–composition isotherm measurements

These were measured by galvanostatic intermittent titration (GITT) with microcurrent [4]. After five charge–discharge cycles to stabilize the SEI film, the anodes were charged at 5 mA/g to 0.0 V, and then further charged potentiostatically at 0.0 V for 2.0 h. Following this, the anodes were discharged under GITT conditions in a series of intermittent discharges at 5 mA/g for 1.0 h, leaving the electrode at open circuit for 2.0 h between each discharge. The amount of extracted Li from graphite (m in Liₙ₋ₓCₐ) in each intermittent discharge was 0.0134 ((72 × 5)/26,800). The open-circuit potential after 2.0 h relaxation as a function of Li content was obtained. The open-circuit time between successive discharge steps was determined to be rather critical, since it must be sufficiently long to establish equilibrium, but short enough so the self-discharge was not significant. To verify that a 2.0 h relaxation time was sufficient to establish equilibrium, the characteristic potentials (the potentials at the start and end of successive stage transformations, i.e. the potential at the start and end of each potential plateau) in the potential–composition isotherms measured using GITT were compared with the characteristic potentials during open circuit in the self-discharge measurement. The characteristic potentials were the same in both cases, confirming that potential–composition curves obtained using GITT represent equilibrium potential–composition isotherms. In fact, GITT had been successfully used to measure the reversible potential as a function of Li content in graphite [5].

2.3. Self-discharge measurement of JM 287 graphite

After charging at 5.0 mA/g to 0.0 V, the graphite electrode was disconnected, and the open-circuit potential of graphite electrode as a function of time was monitored using the Arbin cycler.

3. Results and discussion

3.1. Self-discharge of JM 287 graphite after the first charging to 0.0 V

Fig. 1 shows the open-circuit potential (OCP or equilibrium potential)–composition isotherms (OCP versus x in LiₓCₐ) measured by GITT during the sixth Li extraction cycle after full Li insertion following the above procedure, as well as the open-circuit potential as a function of time. Both the OCP in the open-circuit potential–composition isotherms (OCP versus x in LiₓCₐ) and the OCP profiles during open-circuit time in self-discharge measurement show typical Li graphite intercalation compound characteristics, i.e. five stages for Li extraction from LiₓCₐ in the potential range below 0.3 V (Fig. 1b). These are ascribed to five continuous transitions at compositions Li₆ → LiC₁₂ → LiC₁₈ → LiC₂₇ → LiC₃₆ → LiC₇₂ [5]. The three Li extraction potential plateaus at around 89, 126, and 218 mV are exactly the same as a previous study [5]. As stated above, the characteristic potentials in the 2.0 h open-circuit potential during GITT measurements are the same as those of the open-circuit potential profile during self-discharge, which confirmed that potential–composition curves obtained using GITT represent equilibrium potential–composition isotherms. To obtain the self-discharge rate, the open-circuit potential (OCP) during self-discharge measurement was expressed as the Li content in graphite based on the OCP (or equilibrium potential)–composition isotherms, which allows Li retention to be obtained as a function of open-circuit time. In other words, according to the OCP–composition isotherm curve, we can get the Li content in graphite (x in LiₓCₐ) at a certain OCP. Therefore, the OCPs in OCP versus OCT curves during the self-discharge measurements can be the change in Li content x, i.e. the Li content x versus OCT curves can be obtained. For example, after 85 h, the open-circuit potential in the self-discharge potential profile is 0.09 V, corresponding to the composition Li₅₀.₈C₉₀. The Li retained as a function of time on open-circuit time shown in Fig. 2. The instantaneous self-discharge rate (Fig. 3) may be obtained by differentiating the Li content in Fig. 2 with respect to open-circuit time. The self-discharge rate in Fig. 3, shows three peaks in three single phase regions and low values in the stage transformation regions. The intensities of the peaks in the single phase region decreased with open-circuit time.

The self-discharge performance of graphite anodes may be explained by the growth of the SEI film on the graphite
particles. Li loss from graphite while on open-circuit results from parasitic reactions between intercalated lithium and the electrolyte. The first explanation of the reduced film growth during self-discharge was given by Peled [6]. He ascribed it to the progressively smaller electronic conductance of the SEI film as growth proceeds. The low-solubility SEI film is only a fraction of a micron in thickness [1], and consists of an inner layer of largely inorganic material (Li$_2$CO$_3$, with some LiF from the solute), and an outer rather porous layer consisting of a graded mixture of inorganic material, alkyl lithium carbonates, and polymeric hydrocarbons [1,7,8]. This may be characterized by a Li$^+$ concentration gradient from 57 M (as Li$_2$CO$_3$) at the inner-to-outer layer boundary to 1 M in the electrolyte. When completely formed, the inner layer has the property of conducting some unsolvated Li$^+$, but it probably cannot conduct solvated Li$^+$. The outer layer has progressively smaller Li$^+$ conduction, and greater conduction of solvated Li$^+$, with increasing distance. The mechanism of film formation from the generic carbonate ester solvent AO(CO)OB, which may or may not be cyclic with AB joined, requires the transfer of one electron to produce the first alkyl carbonate ion product, AO(CO)O$, plus the free radical B$. This is followed by a second similar electron transfer to form CO$_3^{2-} + A^*$. Combination of the free radicals yields the polymeric material. The source of the electrons is via discharge of Li atoms to Li$^+$ at the electrode.

Fig. 1. (a) Solid line: open-circuit potential of a JM 287 graphite anode as a function of time on open circuit after the first complete charge to 0.0 V at 5 mA/g at 25 °C; dashed line: open-circuit potential (equilibrium potential)–composition isotherms measured at 25 °C using the GITT technique with successive discharges at 5 mA/g for 1.0 h followed by 2.0 h on open circuit. (b) Enlarged part of (a) in the stage transformation region to show the characteristic stage-transformation potential.
Fig. 2. Li retention in JM 287 graphite as a function of time on open circuit after the first complete charge to 0.0 V at 5 mA/g at 25 °C.

surface, but a means must be sought for their transfer from the surface to the point where the carbonate ester or alkyl carbonate ion becomes available. Electron tunneling through the primary layer has been suggested as a probable mechanism for transfer to that point [7]. However, some means of transfer to the point at which reactants are available is required. A further point is the nature of the reactant itself. Carbonate ester coordinating Li⁺ would be expected to be less stable than the free solvent molecules, because of electron displacement to the carbonate end of the molecule via the induced dipole effect. In addition, the positive charge on the solvated ion would represent a more favorable target for electrons. However, the free radicals should readily be able to accept electrons, giving carbonions. Thus, the reaction may proceed via a pool of free radicals carrying electrons from the surface, where they react with solvated lithium as in the following example (only one ligand is shown, since the others detach after charge-transfer):

\[ \text{Li}[\text{AO(CO)OB}]^+ + \text{A}^- \rightarrow \text{Li}[\text{AO(CO)O}] + \text{A}^* + \text{B}^* \]

Following this step, the free radicals may polymerize, or carry electrons from the surface. This explains how a free radical pool occurs, since two are produced per electron transfer. The insoluble product also forms in situ, and does not require diffusion of positive and negative ions towards each other. Further, the detached ligands form a pool for solvation of the Li⁺ produced by the electron transfer at the graphite surface, which passes through the outer film into the electrolyte. Finally, slightly soluble alkali carbonate ion is further oxidized in similar steps on the surface of the inner

Fig. 3. Self-discharge rate for JM 287 graphite anode obtained by differentiating Li content with respect to open-circuit time from the data in Fig. 2.
film. This provides a reasonably consistent model of film growth. The passivating inner layer controls the flow of electrons, which is the rate-determining step overall.

The Li loss process includes: (i) Li diffusion in the graphite particle, (ii) movement of the Li phase boundaries from the edges to the particle center, (iii) the ionic and electronic mobilities of Li\(^+\) and electrons in the SEI layer [9]. As a first approximation, the electronic mobility of Li\(^+\) in the SEI layer is proportional to the SEI electronic conductance \(X\) [1]:

\[
\frac{dx}{dt} = kX = \frac{k_2 s}{l_0 + A x}
\]

(1)

where \(x\) is the number of moles of Li being reacting, \(z\) the specific conductivity, \(s\) the interface area, \(l_0\) the initial layer thickness, \(A\) and \(k\) are coefficients. Eq. (1) indicates that if the self-discharge rate is limited by the SEI electronic conductance, then its rate should decrease with time on open circuit [1]. Since the peak intensities for self-discharge in the single phase region do indeed decrease with time on open circuit (Fig. 3), this indicates that graphite anode self-discharge is controlled by growth and thickness of the inner SEI film. The low self-discharge rate in the phase transformation region indicates the phase transformation barrier decreases the self-discharge rate because the stage transformation has been confirmed as the rate-limiting step of Li extraction from graphite [4]. A difference in the self-discharge rate in the single- and two-phase regions has been reported by Broussely et al. [1], who considered it due to random scattering of the experimental results. A low self-discharge rate in the two-phase region cannot be attributed to a slow change of potential with time, because large composition changes occur over small ranges of potential in the flat plateau region.

The advantage of the proposed method of measurement of self-discharge is that it can give details of the self-discharge rate within the different stage regions by simple measurement of the open-circuit potential as a function of time in comparison with the equilibrium potential–composition isotherms.

3.2. The self-discharge rate of JM 287 graphite after five charge–discharge cycles

If the decreasing self-discharge rate is largely dependent on the growth of the SEI film, self-discharge should be much lower after five charge–discharge cycles, i.e. when the passivating SEI film is completely formed. Fig. 4 shows the open-circuit potential of a graphite anode as a function of time on open circuit after five charge–discharge cycles. The open-circuit potentials (or equilibrium potentials) versus Li composition in graphite is also shown for comparison. The time for the variation of open-circuit potential from 0.0 to 0.3 V after the sixth complete charge to 0.0 V is around 15.00 h (Fig. 4), which is almost three times longer than that after the first complete charge to 0.0 V (Fig. 1b). The amount of Li retained after different times on open circuit was obtained by the method described earlier and is shown in Fig. 5a. The self-discharge rate was calculated by differentiating the Li content with respect to time on open circuit (Fig. 5b). In contrast to the self-discharge rate after the first charge as shown in Fig. 3, the peak intensity of the rate of

![Fig. 4](image_url). Solid line: open-circuit potential of JM 287 graphite anode at different open-circuit times after the sixth complete charge to 0.0 V at 5 mA/g at 25 °C. Dashed line: open-circuit potential (Equilibrium potential)–composition isotherms measured at 25 °C using the GITT technique as in Fig. 1.
self-discharge in the single-phase region does not decrease with time spent on open circuit and the self-discharge rate in the \( x \approx 1 \) (Li_{1}C_{6}) single-phase region is even lower than that in the following stage transformation (Li_{1}C_{6} \rightarrow Li_{0.2}C_{6}) region. This behavior may be associated with (i) the coupled processes of reductive solvent decomposition and dissolution of the largely soluble products in the electrolyte (insoluble products result in a loose and resistive SEI film [10], (ii) side reactions with electrolyte impurities, (iii) other irreversible reactions, such as disintegration of graphite particles after shrinkage during Li extraction.

The self-discharge rate of graphite electrode in 1 M LiPF_{6}/EC + PC + DMC (1:1:3) electrolyte reported here was much higher than that observed in practical batteries [11]. This may result from: (i) the high concentration of electrolyte PC, which is more reactive than other carbonates on graphite, and (ii) the use of flooded electrolytes.

Since the capacity of graphite anodes will decline due to the disintegration resulting from repeated expansion/con-}

traction and more resistive SEI film growth between particles, the Li content in Li extraction equilibrium potential–composition isotherms will decrease with increasing charge–discharge cycles. However, the change in capacity of the graphite anode during cycling will not influence the characteristic potentials in OCP (or equilibrium potential)–composition isotherms. Hence, the reduction in capacity means that the equilibrium potential–composition isotherms used for self-discharge rate calculation should be measured in the Li extraction cycle just before self-discharge measurement. For simplification, the actual Li content in the equilibrium potential–composition isotherms at any cycle can be approximately calculated by using a modified coefficient \( \lambda \) (Li_{0.2}C_{6}) in the standard equilibrium potential–Li_{0.2}C_{6} curve. The coefficient \( \lambda \) can be approximately obtained by the ratio of charge capacity at very low applied current before self-discharge measurement to the theoretical capacity of graphite (372 mAh/g) if the Coulombic efficiency is considered to be close to unity.

Fig. 5. (a) Li retention in JM 287 graphite after different times on open circuit; (b) self-discharge rate for JM 287 graphite anode after the sixth complete charge to 0.0 V at 5 mA/g at 25 °C.
4. Conclusions

The self-discharge rate of Li-ion graphite anodes can be calculated in a simple manner from the open-circuit potential as a function of time on open circuit using the equilibrium potential–composition isotherms. The self-discharge rate measured by this means can give a detailed picture of the self-discharge rate and Li content in the different stage regions. The self-discharge rate of graphite anodes after the first charge is controlled by the growth (i.e. effective thickness) of the SEI film, although phase transformation from a Li-rich to Li-poor stage decreases the self-discharge rate.

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