Safety and durability are major challenges for commercial lithium-ion batteries (LIBs), especially those used in electric vehicles and large-scale energy storage systems. Herein, we investigate the reliability and degradation behavior of graphite anodes using a LiFePO₄/graphite three-electrode pouch cell. The electrochemical impedance spectroscopy (EIS) and assisted scanning electron microscopy (SEM) results demonstrate the presence of an uneven solid electrolyte interphase (SEI) that grows with prolonged cycling at current rates greater than 1 C. In addition, we provide a direct way to visually detect metallic lithium deposition on graphite anodes by energy dispersive X-ray (EDX) spectroscopy. The three-electrode potential and EDX analyses indicate that metallic lithium deposition begins only after 100 cycles at 1 C, leading to capacity decay and the safety issue of LIBs. Evaluating the characteristics of graphite anodes in rechargeable batteries will provide straightforward guidance for the development of commercial LIBs.

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**Experimental**

**Three-electrode pouch cell.**—All electrochemical experiments were carried out using three-electrode pouch cells. Artificial graphite (FSN-1 from Shanshan Tech Co., Ltd.) was adopted as the anodic active material, and commercial LiFePO₄ (Aleece Eco Ark Co., Ltd.) was used as the positive counter electrode material. A metallic lithium slice was used as the reference electrode and was cemented on a copper wire and placed between the cathode and anode, which were divided by separators. A schematic of the three-electrode pouch cell is shown in Figure S1. The graphite anodes were prepared using a slurry containing 94 wt% graphite active material, 3 wt% carbon black, and 3 wt% PVDF, which was spread onto a copper foil current collector. For the LiFePO₄ cathode, the electrodes were prepared by spreading a mixed slurry containing 92.5 wt% LiFePO₄ active material, 4 wt% carbon black, and 3.5 wt% polyvinylidene fluoride (PVDF) onto an aluminum foil current collector. As shown in Figure S2, after drying and rolling, the electrodes were cut into rectangles with a length and width of ~85 mm and ~50 mm, respectively. The length and width of the anodes were 2 mm larger than those of the cathodes for security purposes. The loading densities of the LiFePO₄ cathode and graphite anode were approximately 8.0 and 7.5 mg cm⁻², respectively. The electrolyte consisted of 1 mol L⁻¹ LiPF₆ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) (1:1:1 volume ratio).

**Electrochemical measurements.**—The electrochemical testing was performed on a LAND CT2001A model battery test system (Wuhan Jinnuo Electronics, Ltd.). All pouch cells were initially activated by 5 cycles at a small rate of C/25 and a cutoff voltage from 2 to 3.65 V. After activation, the pouch cells were charged/discharged at various C rates (0.2 C, 1 C and 10 C). The corresponding current density for 0.2 C, 1 C and 10 C were calculated based on the cathode active material. Three-electrode EIS measurements of the cell in the fully charged state were carried out with an electrochemical work station (Gamry Reference 6000, Gamry Co., USA). The amplitude of the AC perturbation signal was 5 mV, and the frequency range was varied from 100 mHz to 100 kHz. The cells were equilibrated for 24 h before the EIS measurements to reach steady-state conditions. The graphite anode was used as the working electrode, and the morphology evolution of SEI films was influenced by many factors. Andersson et al. revealed that electrolyte solvents more easily decompose at high temperatures. Ota et al. reported that under a high current density, the inorganic components of an SEI form first, and then, the organic components form, which is contrary to the phenomenon observed at a low current density.

To further explore the effect of the graphite electrode/electrolyte interface on the capacity degradation and failure mechanism of LIBs, we investigated the passive state of the SEI and the lithium deposition behavior when a LiFePO₄/graphite full cell was operated at various current densities. SEM and EIS analyses were performed to analyze the morphology and electrochemical properties of the SEI film. In addition, a three-electrode system was designed and utilized to examine lithium deposition on the anode surface, and an EDX analysis was carried out to observe the presence of lithium dendrites. This work provides suggestions for current applications and improvement of commercial power LIBs.
physical characterizations.—The recycled graphite electrodes were washed with DMC solvent in a glove box and naturally dried before being transferred from a sealed container to the SEM chamber (FEI Nova Nano SEM 230). The morphology and microstructure of the surface of the graphite electrodes were investigated by SEM. The corresponding EDX result was adopted to confirm the lithium deposition. Specifically, the cycled graphite anodes were transferred into a nitrogen atmosphere for 24 h of storage at room temperature. Since lithium and nitrogen can readily react to form Li3N at normal temperature and pressure, the quantity of metallic lithium can be determined by detecting nitrogen atoms using EDX.17

Results and Discussion

A fresh battery usually needs to undergo an initial activation (i.e., “battery formation”) process for two purposes: i) to form the SEI film on the surface of the anode to stabilize the subsequent cycles and ii) to remove gases produced by the cathode during the activation process.18 Thus, for activation, the fresh LiFePO4/ graphite three-electrode pouch cells were first charged/discharged at C/25 for 5 cycles. The typical activation voltage profiles are shown in Figure 1a. The first charge capacity is significantly higher than that of the following cycles. Additionally, the charge/discharge curves have substantially better repeatability for the 2nd to 5th cycles, implying most of the SEI films form during the initial charging process.19

After activation, the three-electrode pouch cells were cycled at 0.2 C, 1 C and 10 C between 2 V and 3.65 V at full SOC width to demonstrate the influence of the current density on the battery status. The cycling behavior and capacity retention are shown in Figures 1b and 1c, respectively. The initial specific capacity is approximately 155 mAh g⁻¹ at 0.2 C, with approximately 87% capacity retention after 100 cycles. This retention value is slightly lower than that reported in the literature,20–22 which may be due to the structure of the three-electrode batteries. The lithium wafer between the cathode and anode may somewhat affect the capacity of these LIBs.23,24 However, at 1 C, the capacity quickly declines with cycling. After 100 cycles, the capacity decreases to ∼70% of the first discharge capacity. When the current rate increases to 10 C, the cycling performance is different from that at 0.2 C and 1 C. At 10 C, the capacity rapidly degrades during the first 10 cycles, but in subsequent cycles, the capacity remains intact. Apparently, the capacity fading mechanism of LiFePO4/ graphite full cells is different at low and high currents. The negative and positive
As shown in Figure 2, the potential curves of the negative, positive, and full cells are in situ monitored by the three-electrode system at various current rates. For the initial cycles at 0.2 C, lithium intercalation/deintercalation steps are evident and appear as working plateaus at approximately 3.4 V for LiFePO4 and approximately 0.1 V for LiC6 equilibrium with graphite (Figure 2a). However, as the cycle number approaches 100, the anodic lithium insertion plateau (at 0.07–0.11 V) disappears, and the electrode polarization clearly increases. This behavior indicates that an irreversible side reaction continually occurs on the surface of the anode and eventually inhibits the diffusion and storage of Li+ in the graphite anode. However, at a higher current rate of 1 C, as shown in Figure 2b, the electrochemical polarization of the graphite anode is not significant. However, the negative potential decreases to less than 0 V (vs. Li/Li+) after 50 cycles, implying the possibility of lithium deposition on the anode surface. Another potential platform at 0.75 V becomes increasingly evident during cycling at 10 C. The potential platform at 0.75 V is most likely due to the decomposition of the electrolyte to form the SEI on the surface of the graphite anode. Consequently, a very high current density may promote the decomposition of the electrolyte in LIBs. Therefore, the decrease in the cycle capacity of LIBs at a high current density is probably due to the consumption of Li+ caused by electrolyte decomposition and precipitation of metallic lithium on the anode surface.

To further investigate the mechanism of capacity fading in LIBs, EIS was performed with the graphite anode in a fully charged cell at various current densities and different numbers of cycles. Figure 3a shows the typical impedance responses recorded from the graphite electrode after activation at C/25 for 5 cycles. The basic shape of the Nyquist plot of the graphite electrode includes two semicircles and a diagonal line. According to the fitted equivalent circuit (Figure 3b), R1 is the sum of the electrolyte, electrode, and separator resistances. R2 and CPE1 are the resistance and capacitance of the SEI film, respectively, and R3 and CPE2 are the charge-transfer resistance and double-layer capacitance, respectively. W1 is the
Figure 3. (a) Impedance graph of the graphite anode after 5 cycles at C/25; (b) Corresponding equivalent circuit; the impedance curves of the graphite electrode at various rates after 10 cycles (c) and 100 cycles (d). (○: measured; —: fitted).

Warburg impedance arising from the semi-infinite diffusion of lithium ions at the graphite electrode. Figures 3c and 3d show the Nyquist plots of the graphite electrodes subjected to different rates and cycle numbers in the three-electrode LiFePO4||graphite pouch cell system. In addition, the impedance parameters, R1, R2, and R3, and the total resistance (Rtotal) of the graphite anodes at various states are listed in Table I. As shown in Table I, the resistance of the anode cycled at 0.2 C increases with the cycle number. Both the SEI film resistance R2 and the charge-transfer resistance R3 markedly increase. This observation suggests that the electrolyte continues to degrade and uniformly deposit on the surface of the anode during longtime charge/discharge processes at a low current rate of 0.2 C, which will increase the electrochemical polarization of the anode and lead to declining battery capacity. This result well agrees with the electrochemical cycling performance shown in Figures 1b and 1c and Figure 2a. However, at high rates of 1 C and 10 C, the impedance values subtly increase when the graphite anodes undergo prolonged cycling. This behavior seems to be inconsistent with the electrochemical test results, especially at 10 C. This phenomenon is likely due to uneven SEI deposition. Therefore, ex situ SEM was used to further examine the surface morphologies of anodes cycled at different current densities.

Figure S3a shows the SEM images of a commercial graphite electrode prior to any electrochemical treatment. The average diameter of the bulk graphite particles is approximately 5 μm, and the electrode possesses an uneven surface. Figure S3b shows SEM images of a graphite anode activated for 5 cycles at a current rate of C/25. After activation, the surface of the graphite anode is significantly smoother. The corresponding EDX results show that fluorine (11.2 wt%) and oxygen (4.4 wt%) appear on the surface of the graphite anode after activation (Figure S4), indicating that fluorine and oxygen are in the organic/inorganic components (such as LiF, Li2CO3 and (CH2OCO2Li)2) of the SEI film. The initial activation charge-discharge electrochemical curves (Figure 1a) indicate that an SEI film forms on the surface of the graphite electrode after activation.

Figure 4 shows the SEM images of graphite anodes after 10, 50 and 100 cycles at 0.2 C. As shown in Figure 4a, the SEM images of the graphite anode after 10 cycles are similar to those of the anode after activation, and the surface of the anode remains smooth and flat. After 50 charge/discharge cycles, the SEI film is thick (Figure 4b). At higher...
cycle numbers, the thick SEI pieces join and become more compact (Figure 4c). Although the Li$^+$ conductivity of the SEI film is moderate, it is still substantially lower than that of liquid organic electrolytes. Therefore, as the SEI film thickens, the charge transfer impedance of the battery system increases, corresponding to the increase in $R_2$ with the cycle number (Table I). In other words, for cycling at a low current density of 0.2 C, the internal resistance of the battery increases, which increases the electrochemical polarization (Figure 2a) and results in capacity degradation (Figure 1b).

When the current rate increases to 1 C and 10 C, the evolution of the SEI film becomes clear (Figure 5). After charging and discharging for 10 cycles at 1 C, the SEI film starts to present spherical protrusions on the anode surface (Figure 5a). This phenomenon is more evident at 10 C (Figure 5d). Andersson et al. proposed that these small spheres, with a size of approximately 300 nm, that are distributed along the edge of graphite may be crystalline LiF particles. With subsequent cycles, the SEI layer becomes extremely uneven at the high current rates of 1 C and 10 C. Based on the EIS results in Table I, the value of $R_2$ (SEI resistance) at 1 C and 10 C first increases and then decreases. As shown in Figures 5b and 5e, after 50 cycles, the thickness of the SEI film significantly increases, and regional flake distribution is observed on the anode surface. However, when the cycle number increases to 100, the SEI film agglomerates into many large SEI spheres (Figures 5c and 5f), exposing most of the graphite anode surface. Therefore, high current rates tend to destroy the stability of the SEI film, resulting in a decrease in impedance (Table I). The higher potential plateau at 0.75 V in the three-electrode anodic potential curves at 10 C (Figure 2c) indicates that high current densities also have a great influence on the growth of the spherical SEI on the anode and the corresponding decline in the electrochemical capacity.

![Figure 4. SEM images of the graphite electrode surface after (a) 10, (b) 50 and (c) 100 cycles at 0.2 C. (The corresponding upper and lower figures are various magnifications of the same position.)](image4.png)

![Figure 5. SEM images of the graphite electrode surface after various cycles at 1 C and 10 C.](image5.png)
Since the anodic potential at 1 C and 10 C is close to or lower than that of Li/Li$^+$ (Figures 2b and 2c), lithium deposition is more likely to occur on the electrode surface, which is detrimental to battery safety. To investigate the presence of metallic lithium on the surface of the graphite anodes at 1 C and 10 C, EDX mapping analysis was carried out. Considering that lithium atom be directly detected by X-rays due to its low atomic mass, we innovatively placed the cycled graphite electrodes into a N$_2$ atmosphere to cause the following reaction:

$$6\text{Li} \text{(metal)} + \text{N}_2 \rightarrow 2\text{Li}_3\text{N} \quad [1]$$

Because the other components in the anode do not react with N$_2$, we can indirectly determine the presence of Li metal by detecting the corresponding N. As shown in Figure 6, large amounts of metallic lithium precipitate on the surface of the graphite anode during cycling at high current rates. After 100 cycles at 1 C and 10 C, the lithium metal presents a long linear shape and is assembled in a spiral morphology, which is similar to the results reported by Cui. These results combined with the above SEM and EIS analyses indicate that the deposition of lithium metal should be affected by the state of the SEI film on the anode. The dissolution and regeneration of the SEI cause greater nucleation and growth of lithium metal at certain active sites.

**Conclusions**

The electrode/electrolyte interface of the graphite anode during SEI evolution and lithium deposition at various current densities has been investigated in LiFePO$_4$|graphite three-electrode pouch cell systems. The lifetime and safety of the battery are related to the protective SEI film. The emergence of spherical particles shows that large current densities will cause the passivating SEI layer to develop an uneven morphology. This rapid evolution will accelerate the consumption of the electrolyte and lithium ions, affecting the durability of the battery. In addition, the irregular SEI appears to be responsible for the
nucleation and growth of lithium dendrites. According to the three-electrode voltage results and EDX analyses, at relatively high current densities, the graphite anode tends to trigger dendritic lithium deposition due to the instability of the SEI film. In general, the degradation of commercial LIBs can be attributed to the electrochemical reduction process at the anode surface, and the degradation manifests as a continuous increase in the internal impedance, especially the SEI section process at the anode surface, and the degradation manifests as rates.

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References

1. G. E. Blomgren, Journal of the Electrochemical Society, 164, A5019 (2016).
2. T. Yuan, Z. Tan, C. Ma, J. Yang, Z.-F. Ma, and S. Zheng, Advanced Energy Materials, 7, 1601625 (2017).
3. J. Wang and X. Sun, Energy & Environmental Science, 8, 1110 (2015).
4. J. S. Yeoh, C. F. Armer, and A. Lowe, Materials Today Energy, 9, 198 (2018).
5. F. Wu and G. Yushin, Energy & Environmental Science, 10, 435 (2017).
6. C. E. L. Foss, A. M. Svensson, Gallbrekke, S. Sunde, and F. Vullum-Bruer, Journal of Energy Storage, 17, 395 (2018).
7. L. Suo, D. Oh, Y. Lin, Z. Zhao, O. Borodin, T. Gao, F. Wang, A. Kushima, Z. Wang, H. C. Kim, Y. Qi, W. Yang, F. Pan, J. Li, K. Xu, and C. Wang, Journal of the American Chemical Society, 139, 18670 (2017).
8. S. Huang, L.-Z. Cheong, D. Wang, and C. Shen, Applied Surface Science, 454, 61 (2018).
9. D. Lu, J. Tao, P. Yan, W. A. Henderson, Q. Li, Y. Shao, M. L. Helm, O. Borodin, G. L. Graff, B. Polzin, C.-M. Wang, M. Engelhard, J.-G. Zhang, J. J. De Yoreo, J. Liu, and J. Xiao, Nano Letters, 17, 1602 (2017).
10. S. J. An, J. Li, C. Daniel, D. Mohanty, S. Nagpure, and D. L. Wood, Carbon, 105, 52 (2016).
11. P. Lin, C. Li, E. W. Schneider, and S. J. Harris, The Journal of Physical Chemistry C, 118, 8361-8366 (2014).
12. E. Kazyak, K. N. Wood, and N. P. Dasgupta, Chemistry of Materials, 27, 6457 (2015).
13. X. Su, F. Dogan, J. Ilavsky, V. A. Maroni, D. J. Gosztola, and W. Lu, Chemistry of Materials, 29, 6205 (2017).
14. A. M. Andersson and K. Edström, Journal of the Electrochemical Society, 148, A1100 (2001).
15. H. Ota, T. Sato, H. Suzuki, and T. Usami, Journal of Power Sources, 97-98, 107 (2001).
16. M. Tang, P. Albertus, and J. Newman, Journal of the Electrochemical Society, 156, A390 (2009).
17. M. Wu, Z. Wen, Y. Liu, X. Wang, and L. Huang, Journal of Power Sources, 196, 8091 (2011).
18. K. Kumaz, H. Miyashiro, Y. Kobayashi, K. Takei, and R. Ishikawa, Journal of Power Sources, 81-82, 715 (1999).
19. C. F. Lin, Y. Qi, K. Gregorczyk, S. B. Lee, and G. W. Rubloff, Accounts of Chemical Research, 51, 97 (2018).
20. J. Shim and K. A. Streibel, Journal of Power Sources, 119-121, 955 (2003).
21. A. Kvasa, J. Undamplilala, I. de Meaitza, M. Bengoechea, J. A. Blázquez, L. Yate, O. Miguel, and H.-J. Grande, Electrochimica Acta, 215, 238 (2016).
22. R. Mukherjee, A. V. Thomas, D. Datta, E. Singh, J. Li, O. Eksik, V. B. Shenoy, and N. Koratkar, Nature Communications, 5, 3710 (2014).
23. N. Labyedhi, B. Pati, A.-A. E. Mel, and P. M. Vereecken, Journal of the Electrochemical Society, 165, B3184 (2018).
24. F. L. Simon, L. Blume, M. Hanauer, U. Sauter, and J. Janek, Journal of the Electrochemical Society, 165, A1363 (2018).
25. Z. Liao, Z.-F. Ma, Y.-S. He, X.-M. Zhang, L. Wang, and Y. Jiang, Journal of the Electrochemical Society, 152, A1969 (2005).
26. J. R. Dahn, Physical Review B, 44, 9170 (1991).
27. J. Jiang, H. Ruan, B. Sun, L. Wang, W. Gao, and W. Zhang, Applied Energy, 230, 257 (2018).
28. Q. Guo, Y. Han, H. Wang, S. Xiong, S. Liu, Y. Li, C. Zheng, and K. Xie, Ionics, 24, 2601 (2017).
29. H. Buqa, A. Würsig, J. Vetter, M. E. Spahr, F. Krumbeich, and P. Novák, Journal of Power Sources, 153, 385 (2006).
30. S. Zhang, M. S. Ding, K. Xu, J. Allen, and T. R. Jow, Electrochemical and Solid-State Letters, 4, A206 (2001).
31. F. Wang, M. Yu, Y. Hsiao, Y. Tsai, B. Hwang, Y. Wang, and C. Wan, International Journal of Electrochemical Science, 6, 1014 (2011).
32. P. Verma, P. Maire1, and P. Novák, Electrochimica Acta, 55, 6332 (2010).
33. K. Xu, Chemical Reviews, 114, 11503 (2014).
34. Y. J. Zhang, W. Wang, H. Tang, W. Q. Bai, X. Ge, X. L. Wang, C. D. Gu, and J. P. Tu, Journal of the Electrochemical Society, 177, 304 (2015).
35. Y. Li, Y. Sun, A. Pui, K. Chen, A. Vaiionis, Y. Li, G. Zheng, J. Sun, and Y. Cui, ACS Central Science, 4, 97 (2018).
36. F. Shi, A. Pei, A. Vaiionis, J. Xie, B. Liu, J. Zhao, Y. Gong, and Y. Cui, Proceedings of the National Academy of Sciences of the United States of America, 114, 12138 (2017).