Supporting Information

Incorporation of phosphorus into the surface of natural graphite anode for use in lithium ion batteries

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Our approach is to incorporate phosphorus into the surface through a chemical treatment with NH_4PF_6 . For surface modification, a wet-process has been designed and adopted to make sure that phosphorus is uniformly incorporated on the surface of natural graphite. So, stoichiometric amount (3wt%) of NH_4PF_6 was dissolved in deionized water (200 ml) and homogeneously mixed with natural graphite powder. The detailed procedure is described in Fig. S1. Following a sintering process at 400 °C is allowing a decomposition of NH_4PF_6 and facilitating incorporation of phosphorus on the surface of natural graphite. Through a thermal decomposition of NH_4PF_6 , HF gas was generated and attacked the surface of natural graphite, resulting in change of surface microstructure. For comparative purpose, NH_4F was also used to modify the surface of natural graphite as a reference. We could separate out the effect of HF gas etching and phosphorus incorporation on the electrochemical properties of natural graphite.

Fig. S2 show a comparison of morphologies of natural graphite before and after the surface modification with NH₄F and NH₄PF₆ at different magnifications. FESEM observations clearly show the natural graphite investigated in this work has a spherical shape and an averaged particle size of ~15 μ m. Notable morphological change was not observed after the surface modification with NH₄F and NH₄PF₆ as compared in Fig. S2. The surface has been little roughened after the surface modification. It might be caused by the etching due to HF gas and/ or chemical reactions when the salts are decomposed at 400 °C.



Fig S1. A flow-chart for the chemical surface modification with NH₄F and NH₄PF₆.



Fig. S2 Field emission scanning electron microscope (FESEM) images for natural graphite at different magnifications; (a) pristine, (b) surface modified graphite with NH_4F and (c) surface modified graphite with NH_4PF_6 .

To identify a decomposition mechanism of NH₄PF₆, we conducted analysis on the gas using a differential electrochemical mass spectroscopy (DEMS) combined with a thermo-gravimetric analyzer (TGA) for the salt in a temperature range of 100 °C to 400 °C under N₂ atmosphere. It would be helpful to understand what happens on the surface of natural graphite during surface modification. Possible gases generated from the decomposition of NH₄PF₆ were considered and collected as presented in Figure S3. After setting background with N₂ gas for 12 h and the variations of ion current for each gas were recorded with increasing temperature up to 400 °C with a rate of 5 °C min⁻¹. The obtained signal for NH₃ (*m*/*z*=17) was maximized around 230 °C, which is well matched with the starting temperature for the decrease in relative weight of the salt in the TGA profile. In addition, we found a sharp HF evolution from 300 °C. Other possible gases such as PF (*m*/*z*=50) and PF₃ (*m*/*z*=38) were also detected above such temperature. However, we could not get any evidence for F₂ (*m*/*z*=38) and PF₅ (*m*/*z*=146) in our measurement. To conclude, the result supports the decomposition mechanism of NH₄PF₆ as below;³⁰

 $NH_4PF_6(s) \rightarrow NH_3(g) + HF(g) + PF_5(s)$

$$PF_5(s) \rightarrow PF(g) + PF_3(g)$$

At the initial stage of decomposition, NH_3 gas is generated first and then HF gas is evolved with a further decomposition of PF_5 into PF and PF_3 . The HF gas might etch the surface of natural graphite as mentioned in the main text.



Fig. S3 The gas analysis profiles for NH₄PF₆ measured with differential electrochemical mass spectroscopy (DEMS) and thermo-gravimetric analyzer (TGA).



Fig. S4 X-ray photoelectron spectroscopy (XPS) spectra for the phosphorus incorporated natural graphite after 50 cycles; (a) C 1s, (b) P 2p, (c) Li 1s, and (d) Cl 2p.

As a further step to identify the existence of phosphorus as a part of the SEI, we assembled cells with 1M LiClO₄ dissolved in EC/EMC as an electrolyte to avoid confusing on the phosphorus signal arising from the decomposition of LiPF₆. Interestingly, we observed an obvious P 2p spectrum even after 50 cycles, which indicates that the incorporated phosphorus remains as a part of the SEI on the surface of natural graphite without undesirable loss during cycles. There is no change of binding energy and broadness of the P 2p peak after cycling. In addition, Cl 2p and Li 1s spectra arising from the SEI were clearly detected as shown in Fig S4.



Fig. S5 A comparison of differential scanning calorimetric (DSC) analysis profiles for pristine (solid) and surface modified graphite with NH₄PF₆ (dash).

Recently, much attention has aroused on the development of electric vehicle (EV) and battery technology is getting more important for a proper operation of EV. When the batteries are employed in the EV, thermal stability is one of the most important factors to be considered. Considering a fact that the thermal stability of the batteries is highly depending on the electrode materials, the improvement on the thermal property of materials should be made in advance. Fig. S5 shows DSC profiles for the pristine natural graphite and surface modified with NH_4PF_6 . After being charged to

0.01 V vs. Li/Li+, the cells were carefully disassembled in a glove box to measure their thermal properties. It can be seen clearly that the heat flow for an exothermic peak around 120° C, corresponding a decomposition of SEI layer formed on the surface of graphite was decreased after the surface modification with NH₄PF₆. This result also supports that phosphorus incorporation is quite effective to make the SEI more stable at high temperature which is well matched with the result of thermal storage at 80°C for 48 h as mentioned in the main text.

Another important concern is the electrochemical stability of batteries at low temperature to be used in EV. In this regard, we measured Li⁺ acceptability at -20 °C in the main text and additionally provide discharge profiles at different C-rates here. The cells were charged to 0.01 V vs. Li/Li⁺ at room temperature and the discharged at -20 °C. To make sure the testing temperature of -20 °C, the cells are stored in a temperature controlled chamber for 3 h before each discharging. According to a comparison in Fig. S6, we found that the overpotential of both cells was increased when they were discharged at -20 °C compared to the discharge behaviour at room temperature. The surface modified graphite with NH₄PF₆ delivered discharge capacity of 366.8 mAhg⁻¹ with an initial coulombic efficiency of 91.3% when the cell was discharged with a constant current of 0.2C at -20 °C, which are higher than those of pristine graphite (349.4 mAhg⁻¹, 89.9%). When the applied current was increased up to 5C, there is no significant change in the rate-capability but we pointed out that the capacity fading of the natural graphite after the surface modification with NH₄PF₆ is less than those of pristine even at high C-rate. It is evident that our approach to modify the surface of natural graphite allows better thermal stability of natural graphite.



(a)



(b)

Fig. S6 A comparison of discharge profiles at different C-rate under the low temperature of -20 C for (a) pristine natural graphite and (b) surface modified graphite with NH_4PF_6 .